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Contents

		Page
1796.	An improved ice calorimeter—the determination of its calibration factor and the density of ice at 0° C. Defoe C. Ginnings and Robert J. Corruccini. (Price 10 cents)	583
1797.	Enthalpy, specific heat, and entropy of aluminum oxide from 0° to 900° C. Defoe C. Ginnings and Robert J. Corruccini. (Price 10 cents)	593
1798.	Transmission measurements with the Beckman quartz spectrophotometer. Kasson S. Gibson and Margaret M. Balcom. (Price 10 cents)	601
1799.	Mass spectrometer study of the rare gases. Vernon H. Dibeler, Fred L. Mohler, and Robert M. Reese. (Price 5 cents)	617
1800.	Hydrocarbons in the 102° to 108° C. fraction of petroleum. Augustus R. Glasgow, Jr., Charles B. Willingham, and Frederick D. Rossini. (Price 10 cents)	621
1801.	Heats of combustion and solution of liquid styrene and solid polystyrene, and the heat of polymerization of styrene. Donald E. Roberts, William W. Walton, and Ralph S. Jessup. (Price 10 cents)	627
1802.	Torsion of a rubber cylinder. Ronald S. Rivlin. (Price 10 cents)	637
1803.	Compensation of the aperture ratio markings of a photographic lens for absorption, reflection, and vignetting losses. Irvine C. Gardner. (Price 10 cents)	643
1804.	Heat capacities of gaseous oxygen, isobutane, and 1-butene from −30° to +90° C. Paul F. Wacker, Ruth K. Cheney, and Russell B. Scott. (Price 10 cents)	651
1805.	Heats of solution of solid solutions of hexacalcium dialumino ferrite and dicalcium ferrite. Edwin S. Newman. (Price 5 cents)	661
1806.	Relative thickness of lead, concrete, and steel required for protection against narrow beams of X-rays. George Singer, Harold O. Wyckoff, and Frank H. Day. (Price 10 cents)	665
	Index to volume 38 (January to June 1947, Research Papers RP1758 to RP1806).	673

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Research Paper RP1796
Volume 38, June 1947

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An Improved Ice Calorimeter—the Determination of its Calibration Factor and the Density of Ice at 0° C

By Defoe C. Ginnings and Robert J. Corruccini

There has been described an improved Bunsen ice calorimeter that has been constructed for measurements of enthalpy at high temperatures by the "drop" method. The calibration factor of the ice calorimeter has been determined electrically to be 270.37 ±0.06 international joules per gram of mercury, equivalent to 64.631 ±0.014 calories per gram of mercury where 1 calorie = 4.1833 international joule. Using this calibration factor, it is calculated that the density of ice at 0° C and 1 atmosphere pressure is 0.91671 ± 0.00005 gram per milliliter.

I. Introduction

In 1870 Robert Bunsen devised what is now known as the Bunsen ice calorimeter [1].[1] In this device, the heat to be measured is allowed to melt ice that is in equilibrium with water in a closed system, and the resulting volume decrease is determined by means of mercury drawn into the system. The calibration factor, K, of this ice calorimeter (ratio of heat input to mass of mercury intake) is related to the heat of fusion L of ice, the specific volumes of ice, v_i, and water, v_w, and the density of mercury, d_m, by the equation

$$K = L/(v_i - v_w)d_m. \quad (1)$$

This type of calorimeter has several advantages. First, no temperature or electrical-measuring instruments are necessary if the calibration factor is constant. Second, its sensitivity is sufficiently high that it may be used in microcalorimetry. Third, when it is properly used in an ice bath, the heat leak is very small. On the other hand, it has the disadvantages that it must always be used at 0° C and that the volume of the calorimeter system must be constant. There has been some question of the constancy of the calibration factor of the ice calorimeter because of the poor reproducibility of measurements of the density of ice [2]. As the calibration factor depends on the difference in the specific volumes of ice and water at 0° C, a variation of 0.01 percent in the density of ice would introduce a variation of 0.1 percent in the calibration factor. Values of the density of ice reported by various observers are rather scattered. The value given in the International Critical Tables [3] is given a tolerance of about 0.05 percent, corresponding to 0.5 percent on the calibration factor of the ice calorimeter. As this tolerance is many times larger than might be expected, the desirability for electric-energy calibration is evident. The calibration factor apparently has not been determined by the electrical method since 1914. It is the purpose of this paper to describe a modern ice calorimeter (developed for use in measurements of enthalpy at high temperatures by the "drop" method), the determination of its calibration factor by measured electric-energy input, and the investigation of the constancy of this calibration factor under various experimental conditions.

[1] Figures in brackets indicate the literature references at the end of this paper.

II. Experimental Procedure

1. Description of Apparatus

A schematic diagram of the ice calorimeter is shown in figure 1. A central well, A, is provided to receive objects whose enthalpy (heat content) is to be measured. This well tapers in diameter from 1 in. at the top to ¾ in. at the bottom. An electric heater, H, sheathed in a metal tube is soldered on the outside of the well in order to introduce known amounts of heat for calibration

purposes. The lower part of the well is surrounded by two coaxial glass vessels, M, which provide an insulating space between the inner ice-water system and the surrounding ice bath. The vessels are sealed to brass with Apiezon wax. Any change in volume resulting from melting ice in the inner vessel is transmitted to mercury in reservoir R_1 and thence through a valve, V, to a beaker, B, which is weighed to account for the change in the amount of mercury in the calorimeter system. A constant flow of dry carbon dioxide gas up this central well is provided to prevent diffusion of water vapor from above and condensation in the calorimeter. A coil, T, serves to cool the gas to the bath temperature. A specially designed gate, G, prevents transfer of heat from above to the calorimeter along the central well. The apparatus is immersed in an ice bath up to the level, L, in order to minimize heat leak.

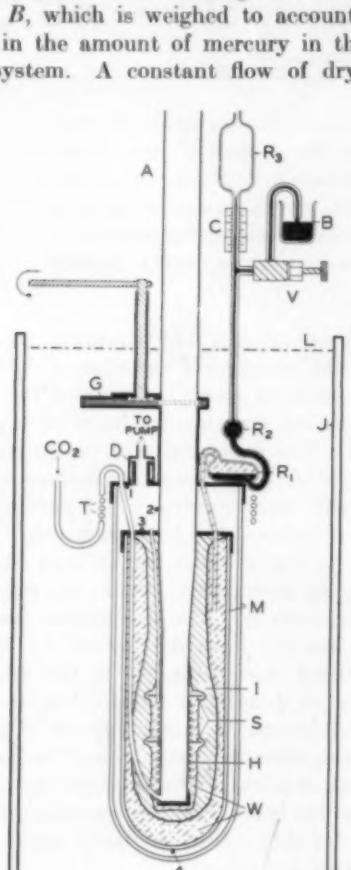

FIGURE 1.—*Diagram of ice calorimeter.*

A, Central well; *H*, electric heater; R_1, R_2, R_3, mercury reservoirs; *V*, needle valve; *B*, weighing beaker; *T*, cooling coil; *G*, gate; *E*, ice bath; *L*, ice-bath level; *I*, ice mantle; *S*, convection shields; 1, 2, 3, 4, thermocouple junctions; *W*, water; *M*, Pyrex vessels; *D*, heat shunt for electric leads; *C*, glass capillary with scale; *J*, Pyrex jar.

2. Filling the Calorimeter with Water

The calorimeter was filled with water that had been distilled in a special still designed to remove about 99.9 percent of the dissolved gases. After the calorimeter system was thoroughly cleaned and evacuated, the air-free water was allowed to flow by gravity down through reservoir R_3, to fill the calorimeter and glass system. After an ice mantle was frozen in the calorimeter, pure mercury was sucked through the mercury valve, V, into reservoir R_3. Melting the ice mantle then brought mercury down into reservoirs R_2 and R_1, while another ice-mantle freezing pushed out any water trapped in R_2. The system above R_3 was then opened to the atmosphere without danger of contaminating the water. The function of R_2 was to trap any air accidentally let into the mercury system and prevent its entry into R_1, where it would contaminate the water. All metal surfaces in the calorimeter were coated with tin so that the water was exposed essentially to Pyrex glass and tin with only a small area exposed to the Apiezon wax. As a check on the upper limit of the amount of impurities in the water in the calorimeter, the water that had been used from July 5 to August 18, 1945, was removed and its electrical conductivity measured. In spite of some contamination during its removal, its electrical conductivity indicated a freezing-point lowering of only a few ten-thousandths of a degree. A check on the purity of the water while it was in the calorimeter was provided by observation of the heat-leak coefficient. As the ice-bath temperature was probably reproducible to a few ten-thousandths of a degree, as indicated by conductivity measurements, any lowering in the calorimeter temperature due to contamination of the water in the inner system would be detected by a change in the heat-leak coefficient. No significant change was observed during the 7-month period one sample of water was in the calorimeter.

3. Description of Ice-Mantle Technic

An ice mantle, I, was frozen around the central well in the inner vessel by introducing a tube filled with solid carbon dioxide into the well. The shape of the ice mantle and the rate of freezing were controlled by adjusting the thermal contact between this tube and the well. The ice mantle was usually frozen in about 1½ hr to approximately the configuration shown in figure 1. With this rate of freezing, no visible cracks in the ice developed during freezing, although some very small "filaments" always developed in the ice after the freezing was stopped. These filaments seemed to go all the way through the ice mantle to the central well and apparently [4] are spaces filled with liquid. Microscopic examination of ordinary ice showed similar filaments that were located at intersections of surfaces of individual ice crystals. As shown in figure 1, the tube connecting the calorimeter with mercury reservoir R_1 extended down into the calorimeter far enough to prevent ice closing the end of the tube. For ordinary rates of freezing, the water in this tube, where it was surrounded by ice, subcooled sufficiently to avoid freezing. Usually, an ice mantle was frozen and allowed to stand overnight before being used, although experiments have shown that this is not necessary if certain precautions are taken. The dimensions of the ice mantle around the lower part of the central well, where most of the heat is dissipated, permit the measurement of about 5,000 calories before the mantle melts through. Once the ice mantle has melted through, the calorimeter no longer accurately accounts for heat supplied to it as the warm water escaping to the outside of the pierced mantle then loses some of its heat to the outer ice bath.

The shields, S, served to reduce convection in the liquid water next to the central well and thereby distribute more evenly the melting of the ice. It would be advantageous to utilize a system of heat-diffusing metal vanes in the calorimeter so that the heat might travel more quickly to the inner ice surface. As the calorimeter is now constructed, the time required for the calorimeter to come to equilibrium varies from a few seconds when the ice mantle is very close to the central well to about 25 minutes after 4,000 calories have been absorbed. This latter time could probably be reduced to less than 5 minutes with a heat-diffusing system.

With the intent of establishing a fluid connection from the inside to the outside of the ice mantle, it was the usual practice to "premelt" a little ice along the central well and next to the brass lid of the inner system by introducing a tube with warm water into the central well. However, experiments made with no intentional premelting indicate that the response of the mercury meniscus to heat input is immediate in spite of no apparent liquid connection between the inner and outer water. This might possibly mean that the ice has been pulled away from the metal or that there is a liquid connection through the filament-like openings in the ice. It is believed that after "premelting", the calorimeter may be used for precise measurements as soon after freezing the ice mantle as thermal and mechanical equilibria are attained, and the calorimeter "drift", or heat leak, has been established. With the present apparatus, the calorimeter seems to be at equilibrium within 1 to 2 hr after freezing the mantle and packing the ice bath, provided no recent mechanical strain has been imposed on the system. An example of such a strain is a change in pressure of 1 atmosphere on the calorimeter system; equilibrium was attained only after at least 2 hr.

4. Description of Accounting for Mercury

The amount of mercury drawn in during an experiment is accounted for mainly by weighing the beaker of mercury. When the valve, V, is closed, the beaker may be removed for weighing and any small change in the amount of mercury measured in a calibrated-glass capillary. The observation of the position of the mercury meniscus in the capillary tube, C, is much easier than weighing mercury when changes are small. The position of the mercury meniscus in this capillary is usually made essentially the same at the end of an experiment as at the beginning. The capillary tube was calibrated in place by weighing the increase in the amount of mercury in the beaker as the mercury meniscus in the tube was lowered. This duplex system of measuring large energies by weighing mercury, and measuring small energies by observing the mercury meniscus in a glass capillary has proved very satisfactory. Before replacing the beaker of mercury, a slight

pressure is applied above R_3 with the valve open, thereby pushing out a small globule of mercury on the end of the tip of the capillary tube. In this way, no air is trapped when the beaker of mercury is brought up around the capillary tip. The glass capillary, which has a bore of about 0.6 mm, is constricted slightly at the tip. The valve consists of a hard steel needle seating upon a soft steel seat, using a paraffin-impregnated leather packing. The valve is designed to contain a minimum of mercury and is always in the closed position when the accounting for mercury is made. Precaution was taken to avoid an air bubble in the valve, which would cause the mercury column in the capillary to break above the end of the capillary as the beaker of mercury was removed. The amount of mercury in the glass capillary and steel valve was small enough so that changes in room temperature would not introduce appreciable error. Experiments described later indicate that the system of mercury accounting was sensitive to the equivalent of a few hundredths of a calorie, corresponding approximately to the precision in observing the position of the mercury meniscus in the glass capillary. In order to utilize this precision, proper precaution must be taken that the ice calorimeter and its mercury connections are rigidly mounted so that there is no appreciable variation in volume of the mercury and water systems due to any other cause than the melting of ice.

5. Heat-Leak Control

The heat leak was maintained small by keeping the temperatures of the calorimeter and the ice bath nearly the same. While barometric pressure was maintained on both the ice bath and the insulating gas space around the calorimeter, the pressure in the calorimeter was about 0.2 atmosphere higher than the barometric pressure due to the head of the mercury column between mercury reservoir R_1 and the mercury meniscus in the glass capillary. The excess pressure about compensates for the elevation of the temperature of the calorimeter due to the absence of air in solution so that the calorimeter is very close to 0° C. The temperature of the ice bath was maintained as close to 0° C as possible by using clear ice and pure water to make up the bath. It was found satisfactory to use the water from the melted ice to make up the bath from day to day. The ice bath was contained in a large Pyrex jar with insulation, part of which could be removed for observation during the freezing of the ice mantle. One packing of the ice bath was sufficient for at least 12 hr, except for the top inch or so, which was repacked frequently. Several thermocouples were installed for detection of temperature changes. One thermocouple, having a principal junction (4 in fig. 1) on the bottom part of the inner-glass container, proved to be useful in detecting if the protecting ice mantle melted through because the warmer water quickly settled to the bottom. This same thermocouple served as a check on the proper maintenance of the top part of the ice bath as the reference junction (1 in fig. 1) of this thermocouple was located on the top lid of the outer vessel. Under actual working conditions, with dry carbon dioxide in the insulating space around the calorimeter, heat was lost from the calorimeter at the rate of about 0.3 cal/hr, corresponding to about 5 mg of mercury, or 0.7 mm change in the mercury height in the capillary. In order to insure dryness, the insulating space was evacuated once a day through a pump connection near D (fig. 1) and filled with dry gas.

In the evaluation of heat leak when the electric heat is on, it is necessary to consider the possibility of heat loss from the calorimeter by conduction, radiation, or convection up the central well. The heat loss by conduction was made negligible by using a central well made of thin (0.25 mm) copper-nickel for low thermal conductivity. This central well was tempered satisfactorily by the ice mantle, so that the temperature of the well at the top of the calorimeter was not affected by heat input at the bottom of the well. The radiation loss was made small by making the well relatively deep. Experiments described later proved that heat loss by radiation and convection was negligible.

As the calorimeter was devised for use in experiments where an object would be dropped into the central well, it was necessary to provide a gate that could be opened for a short time for the dropping, but which normally is closed exposing a surface near 0° C to the central well so that no heat would be radiated down to the calorimeter. The gate, G, consists of a copper disk (about 3 mm thick) that may be rotated inside a brass housing with only a few tenths of a millimeter spacing between the disk and the housing. Any heat received by

he part of the copper disk which is blocking the entral well is dissipated through the gas space and ousing to the outer ice bath. In this way, the emperature of the copper disk is maintained suffiiently close to 0° C so that there is no appreciable adiation down to the calorimeter. The copper isk is coated with a surface of polished tin to ower its emissivity. Experiments indicated hat the gate is completely effective in dissipating adiation energy even when a furnace at 900° C is sed above the calorimeter.

6. Electric-Energy Measurement

The electric heater used in the calibration experiments consisted of 10 ohms of glass-covered No. 34 AWG constantan wire, joined to No. 26 AWG silk-covered enamelled copper wire for current leads, all snugly contained in a thin copper tube about 1.3 mm in outside diameter. The constantan part of the heater was located in a coil, *H*, wound around the bottom 6 cm of the central well; the current leads extended up along the central well through the top lid of the inner vessel to the insulating space between the two vessels where the potential leads were attached. One potential lead was attached close to the inner lid and the other close to the outer lid on the assumption that one-half of the energy developed in the current leads in the space between the lids would pass to the calorimeter. From the resistance of the current leads, it was computed that about 0.05 percent of the total energy input to the calorimeter came from heat developed in the current leads in the insulating space. Both power and thermocouple leads going to the insulating space from the outside were brought through a tube to a heat shunt, *D*, where they were wound in good thermal contact with the metal for a length of 10 cm. In this way, any heat conducted from room temperature was dissipated to the ice bath. The measurements of electric power and time were made similar to those of Osborne, Stimson, and Ginnings [5].

III. Results

1. "Apparent" Calibration Factor

The results of the electric-calibration experiments made from July 28, 1945, to May 21, 1946, are given in table 1. In column 3 the mass of mercury listed is the difference in the weights of the beaker of mercury at the beginning and the end of the experiment, corrected for buoyancy, and also corrected for the heat leak and change in the position of the mercury meniscus in the glass capillary during the experiment. This last correction averaged only about 0.5 j and is not listed separately. In column 5, is given the total time of the experiment, that is, the time between the observation of the amount of mercury just before the start of the experiment and the similar observation when the calorimeter is considered to be at equilibrium. In column 6 is given the calibration factor, that is, the electric energy divided by the corrected mass of mercury. In column 7 are given any changes in experimental manipulation that were made to detect experimental errors and to determine if the calibration factor of the ice calorimeter was independent of certain variables. If nothing is given in column 7, the usual experimental manipulation was followed, consisting in freezing the ice mantle in about 1.5 hr, premelting a little ice around the central well, and using an electric power of about 7 w and a carbon dioxide flow rate up the central well of about 0.1 ml/sec.

Examination of table 1 shows that there are two main types of experiments, those with energies from 8,000 to 17,000 j, and those with energies of about 800 j. The large-energy experiments were made to minimize small absolute errors in energy and therefore give the best value of the calibration factor, while the small-energy experiments were made to detect any small absolute error that might be significant only in this type of experiment. The small-energy experiments of March 13, 14, and 15 gave the same result as the average of the large-energy experiments of February and March, indicating that no significant error of this type existed. It is interesting to note that the average deviation from the mean for these 800-j experiments was about 0.04 j/g, or about 0.1 j, which corresponds to about 0.02 mm on the height of the mercury meniscus in the capillary tube. No attempt was made to observe the position of this meniscus closer than the nearest 0.05 mm. It should also be noted that all small-energy experiments were made by using the part of the ice mantle close to the central well. Under these conditions, the time for the calorimeter to come to equilibrium is only a few minutes.

TABLE 1.—*Results of electrical calibration experiments*

Date	Heat leak	Mass of mercury	Electric energy	Time	Calibration factor	Variations in experimental manipulation
1945	*Int. j*	*g*	*Int. j*	*min*	*Int. j/g*	
July 28	4.6	45.3045	12249.1	63	270.37	
Aug. 1	0.6	45.5712	12319.2	66	270.33	
3	1.7	39.4351	10660.2	59	270.32	
4	0.6	60.5326	16367.9	64	270.40	
11	.0	51.1239	13823.0	62	270.38	
20	.6	60.1702	16267.5	69	270.36	Water in calorimeter changed.
Oct. 16	1.0	33.0416	8933.0	46	270.36	Water in calorimeter changed again.
16	1.2	33.0227	8927.1	64	270.33	
Nov. 2	1.3	55.7218	15064.9	85	270.36	Electric power input 1.7 larger than usual.
13	0.6	56.3255	15231.5	70	270.42	Ice 40 hr old instead of usual 17 hr.
15	3.6	52.4115	14169.7	101	270.35	Extra time due to capsule in calorimeter.
19	1.2	61.5785	16650.9	92	270.40	Ice mantle 5 hr old.
20	1.3	61.6041	16655.7	105	270.37	Ice mantle 3 hr old.
Dec. 18	0.4	61.9147	16739.6	75	270.37	
21	1.0	62.0205	16765.4	69	270.32	Ice mantle 60 hr old.
1946						
Jan. 5	0.06	3.0834	833.85	10	270.43	Ice mantle 4 hr old—no premelting around well.
5	.06	3.0834	833.80	11	270.42	Do.
5	.06	3.0828	833.80	14	270.47	Do.
5	.06	3.0841	833.79	16	270.35	Do.
5	.4	46.2425	12502.6	53	270.37	Do.
9	.10	3.0816	833.55	10	270.49	Do.
9	.10	3.0819	833.49	10	270.45	Do.
9	.10	3.0829	833.49	11	270.36	Do.
9	.10	3.0818	833.40	15	270.43	Do.
9	1.0	46.2339	12499.7	57	270.36	Do.
30	0.9	62.3932	16867.9	69	270.35	Froze ice mantle 5 times usual rate—no premelting.
Feb. 21	.3	61.9732	16752.2	68	270.31	Cotton in central well in calorimeter.
25	.5	59.0118	15951.9	80	270.32	Do.
26	1.0	61.0743	16509.9	76	270.32	Reduced CO_2 flow by one-half—cotton in central well.
28	0.9	44.5959	12058.4	62	270.39	Froze ice at one-fifth usual rate—cotton in well.
Mar. 4	.5	59.4616	16072.3	80	270.30	Cotton in central well.
5	.5	58.8596	15911.1	75	270.32	Reduced CO_2 flow rate to one-third usual rate.
6	.0	60.5402	16366.5	73	270.34	Increased CO_2 rate by factor of 2 (0.16 ml/sec).
8	.4	29.6909	8026.0	45	270.32	Froze ice at one-fifth usual rate—cotton in well.
9	.2	61.9352	16742.4	80	270.32	Low mercury level in reservoir—cotton in well.
11	.5	59.8744	16184.8	75	270.31	Froze ice under less pressure—cotton in well.
12	.6	59.3499	16043.8	79	270.33	CO_2 rate high (0.2 ml/sec)—shine light on ice.
13	.10	2.9555	798.96	10	270.33	
13	.12	2.9558	799.09	12	270.35	
13	.12	2.9565	799.11	11	270.29	
13	.15	2.9567	799.15	15	270.28	
13	.3	44.3087	11976.9	53	270.31	
14	.00	3.0846	833.56	10	270.23	
14	.02	3.0821	833.44	10	270.41	
14	.04	3.0827	833.35	13	270.33	
14	.06	3.0825	833.26	13	270.32	
14	.1	46.0957	12458.9	44	270.28	Electric power 1.7 higher than usual.
15	−.10	2.9840	806.83	11	270.39	No premelting around well.
15	−.08	2.9847	806.79	11	270.31	Do.
15	−.04	2.9853	806.83	11	270.27	Do.
15	.00	2.9844	806.77	12	270.33	Do.
15	.8	47.0496	12716.8	79	270.28	Electric power input 0.56 of usual—no premelting.
Apr. 22	.5	60.8300	16444.8	72	270.39	New power—measuring instruments used.
23	.2	60.6033	16387.1	71	270.40	Do.
May 14	.3	57.4830	15544.7	72	270.42	Do.
17	.4	63.9209	17283.3	70	270.39	Do.
20	−.2	63.7193	17229.2	72	270.39	Do.
21	.0	63.6903	17222.9	73	270.42	Do.

The small-energy experiments of January 5 and 9 were made with the ice mantle frozen only about 4 hr before the experiment and with no previous melting of the ice mantle next to the central well. These experiments indicated that about 0.02 percent error might be introduced under these conditions in the first few thousand joules of energy input. It should be noted that in the small-energy experiments of March 15, where no ice was previously melted next to the central well, the time interval after the freezing of the mantle eliminated most of this small error.

Of the large-energy experiments, those of November 2, March 14 and 15 were made varying the electric power by a factor of about 3. In the experiments of November 13, 19, 20, December 21, January 5 and 9, the age of the ice mantle was varied from about 3 to 60 hours. In the experiments of January 30, February 28, and March 8, the rate of freezing of the ice mantle was varied by a factor of about 25. From February 21 to March 6, a study was made of the possibility of loss of heat from the calorimeter up the central well, either by the carbon-dioxide flow or by radiation. The carbon-dioxide flow was varied from about 0.03 to 0.2 ml/sec, and any radiation was blocked by introducing a plug of cotton down the central well in the region just above the heater. The effect of not premelting a little ice around the central well was studied on January 5, 9, and March 15. On March 13 an experiment was made with a mantle that had been exposed to bright light for about 15 minutes, on the possibility that melting between crystals in the ice might affect the calibration factor. The experiments were made with three different charges of water in the calorimeter, the first in the calorimeter from July 4 to August 18, the second from August 19 to September 12, and the third from September 13 through the end of the experiments. On March 11 an experiment was made with an ice mantle frozen under about 0.2-atmosphere pressure instead of the usual 1.2 atmospheres. On March 9 an experiment was made with the level of mercury in reservoir R_1 much lower than usual in order to check that the change in level of the mercury during an experiment was sufficiently constant.

It is believed that none of the experimental variations described had any significant effect on the calibration factor, with the one exception previously mentioned that when an ice mantle is used within a few hours after being frozen, it may be desirable to premelt some of the ice around the central well. This is in contrast with Stern [6], who reports that it was about 4 days after freezing the mantle before the calorimeter was at equilibrium.

In connection with the experiments with old ice mantles, there should be mentioned a few experiments made in July 1945, in which quantities of heat from 800 to 2,400 j were put into the calorimeter in "drop" experiments by using ice-mantles that were 2 and 3 days old. These experiments gave results that were about 0.2 percent lower than experiments with ice mantles that were 1 day old. However, observations of the thermocouple (No. 3) on the upper part of the calorimeter, as well as observations of the time for the calorimeter to come to equilibrium in the morning, indicated that the reason for this behavior lay in the failure to maintain a protecting ice mantle in the upper part of the calorimeter. Because of the hot weather, one overnight packing of the ice bath did not prevent considerable heat flow to the top of the calorimeter. This melted so much of the ice in the top part of the calorimeter overnight, that during the experiments there was not enough ice to prevent loss of some of the heat at the top. In the electric-calibration experiments, precaution was taken that the part of the ice mantle in the top of the calorimeter was still intact.

It will be noted that the results show a downward trend in February and March. The explanation of this trend was found in tests on March 19 to 21, which showed that the calibration of the potentiometer used to measure power had changed since the last determination in November 1944 by about 0.013 percent, affecting the power readings by 0.026 percent. After adjusting the values in table 1 for July 28, 1945, through March 15, 1946, to allow for the potentiometer recalibration, the results prior to April 1946, gave an "apparent" calibration factor of 270.38 int. j/g of mercury. In April and May 1946, experiments were made by using different power-measuring instruments, including a new and more dependable potentiometer. These experiments gave an "apparent" calibration factor of 270.40, which was considered more reliable than the earlier value.

2. "Ideal" Calibration Factor

In the ice calorimeter described the level of mercury in reservoir R_1 rises slightly during each experiment, thereby lowering the pressure on the calorimeter. As the calorimeter system is not ideally noncompressible, this change in pressure produces a change in volume that must be accounted for in order to obtain the "ideal" calibration factor where the pressure remains constant. By observing the response of the meniscus to changes in pressure above R_3, it was found that a change in pressure on the system of 1 mm of mercury changed the height of the mercury in the capillary by 0.27 mm. Taking this compressibility and the observed change in level of the mercury in R_1 during an experiment (about 3 mm for 16,000 j), it is computed that the value of the calibration factor should be reduced to 270.37 int. j/g of mercury. The effect of the small accidental variation of the height of the mercury meniscus in the glass capillary is negligible as the method of calibrating the capillary takes into account the compressibility of the system, and the change in temperature of the calorimeter is negligible for the small pressure changes. Also the calibration factor for 1.0-atmosphere pressure would be essentially the same as for 1.2 atmospheres. Therefore the final value for the calibration factor of the ice calorimeter is taken as 270.37 int. j/g of mercury (equivalent to 64.631 cal/g of mercury when 1 cal=4.1833 int. j). The authors estimate the uncertainty in this value to be about ± 0.06 int. j/g. This estimate is based mainly on the uncertainty in the accounting for heat developed in the calorimeter heater leads.

IV. Comparison of Results With Others

Prior to 1900 most experimenters determined the calibration factor of the ice calorimeter in terms of the heat capacity of water. The results of these determinations are not given here as they are not as accurate as those from electric calibration experiments. In recent years most experimenters in ice calorimetry have been satisfied with moderate accuracy in the measurements of small amounts of heat. These experimenters have therefore accepted the calibration factors given in earlier work. The most trustworthy of the determinations of the calibration factor appear to be those of Dieterici [7] in 1905 and Griffiths [8] in 1913, both made by electrical means. Dieterici made 10 calibration experiments of about 300 j each, with an average deviation from the mean of about 0.07 percent. After correction for changes in electrical standards to those now in use, his calibration factor is 270.49 int. j/g ± 0.14. Griffiths made 12 experiments of about 1,000 j each with an average deviation from the mean of about 0.09 percent. His calibration factor was 270.18 int. j/g, which he regarded to have a probable error of 0.08 percent (± 0.22 int. j/g). The value of 270.37 int. j/g from the present report is within the respective tolerances of both Dieterici and Griffiths.

V. Density of Ice

Using eq 1, the density of ice at 0° C and 1-atmosphere pressure may be calculated from the calibration factor of the ice calorimeter, the heat of fusion of ice, and the densities of water and mercury. Using 270.37 int. j/g of mercury for the calibration factor, 0.999868 g/ml for the density of water, 13.5955 g/ml for the density of mercury, and 333.5 int. j/g [9] for the heat of fusion of ice, the density of ice at 0° C and 1-atmosphere pressure was calculated to be 0.91671 g/ml. The largest uncertainty in this calculation is believed to be caused by the uncertainty of 0.06 percent in the heat of fusion of ice, which is equivalent to 0.00005 g/ml in the density of ice.

The numerous measurements of the density of ice have been reviewed by Dorsey [2]. The results of these measurements have been so scattered that some observers have believed the density of ice to be not strictly constant. The value given in the International Critical Tables [3] for the density of ice at 0° C and 1-atmosphere is 0.9168 ± 0.0005 g/ml. It is believed that the ice calorimeter method provides the most accurate determination of this constant since this method is free from many of the difficulties inherent in other methods. On account of the filaments and cracks that all samples of ice appear to have, any experimental method that measures the "bulk" density of ice will obviously give a different result from methods, such as the present one, which determine the true density. Finally, no evidence has been obtained with the ice calorimeter that the true density of ice is anything but constant.

VI. Summary

1. There has been described an improve ice calorimeter that has been used in determinations of enthalpy at high temperatures by the "drop" method.

2. Electric-calibration experiments with this calorimeter indicate that the ice-calorimeter calibration factor is constant within the precision of the experiments under a variety of experimental conditions.

3. The calibration factor of the ice calorimeter has been determined to be 270.37 ± 0.06 int. joule per gram of mercury, equivalent to 64.631 ± 0.014 cal/g of mercury, where 1 cal=4.1833 int. j.

4. From this calibration factor, the densities of water and mercury, and the heat of fusion of ice, it is calculated that the density of ice at 0° C and 1 atmosphere pressure is 0.91671 ± 0.00005 g/ml.

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Enthalpy, Specific Heat, and Entropy of Aluminum Oxide from 0° to 900° C

By Defoe C. Ginnings and Robert J. Corruccini

Apparatus consisting of a furnace and ice calorimeter has been used for the measurement of enthalpies at high temperatures by the "drop" method. The enthalpy (referred to 0° C) of a sample of aluminum oxide (corundum) has been determined in the range 0° to 900° C. Derived values of specific heat and entropy are given.

I. Introduction

Substances whose thermal properties are accurately known are frequently useful in calorimetry. For example, benzoic acid is used in combustion calorimetry for determining the so-called energy equivalent of the calorimeter. This avoids electric-energy calibration of the calorimeter and, being a substitution method, eliminates those experimental errors that remain the same in all combustion experiments.

Similar use of a substitution method in heat-capacity measurements may be convenient in some cases, especially with calorimeters used in the method of mixtures. Here, the energy equivalent of the calorimeter would be determined by experiments with a standard substance having accurately known heat capacity.

More often, perhaps, observers would find it desirable to utilize experiments with the standard substance to give an indication of the accuracy obtained by them and to provide a guide toward improvement of instrumental technic. In the past, water, because of the many accurate investigations of its properties, has served these functions more often than any other substance.

A material whose enthalpy and heat capacity were accurately determined over a very much larger temperature range than is possible with water would constitute a desirable calorimetric standard substance. This material would preferably be a crystalline solid without transitions or changes of state up to, say, 1,600° C. It should be nonvolatile, nonhygroscopic, chemically stable in air, and should not absorb carbon dioxide. It also should be of high purity, and the uncertainty involved in correcting the results for the impurities should be considerably less than the error of the accurate thermal data that would establish the substance as a standard. The heat capacity per unit volume (specific heat times density) should be high. There is ample evidence that introduction of mechanical effects, such as strains due to cold-working, cause small but appreciable changes in the thermal properties of metals. Hence it seems desirable at present to eliminate malleable substances, including most metals, from the list of prospects.

Among the most promising possibilities, then, are the oxides of Be, Mg, Al, and Zr, provided they are not so finely divided as to adsorb moisture from the air. This paper presents the results in the range 0° to 900° C of an investigation that was undertaken to determine the suitability of α–Al_2O_3 (corundum)[1] for use as the above-mentioned standard substance, this material having been tentatively chosen because of its commercial availability in high purity.

II. Experimental Procedure

1. Sample

The sample of Al_2O_3 was synthetic sapphire obtained from the Linde Air Products Co. in the form of polished rods, 2.5 mm in diameter and 36 mm long. The weight of the sample used was 8.0406 g, corrected for buoyancy. A spectrographic

[1] The so-called β-form is an impure alumina, whereas the γ-form, prepared from precipitated alumina, is metastable, transforming to corundum at about 1,000° C.

analysis performed after the completion of the heat measurements indicated 0.02 to .03 percent impurity. No correction for the impurity was applied as it was largely SiO_2, which, in this temperature range, has a specific heat very close to that of Al_2O_3. It seems probable that the specific heat of this sample was the same as that of the pure material within less than 0.01 percent. A 1.4–g portion of the sample was ignited at 1,000° C for 1 hour without detectable loss of mass (0.1 mg).

2. Apparatus

The apparatus, shown in figure 1, consisted essentially of a furnace and an ice calorimeter. The sample (contained in a sealed capsule) was heated to a known temperature in the furnace and dropped into the calorimeter that measured the heat evolved in cooling the sample to 0° C. The heat content of the empty capsule, together with the small heat loss during the drop, were accounted for in separate "blank" experiments. The ice calorimeter is described elsewhere [1].[2]

The furnace was mounted in such a way that it could be swung aside from its position over the calorimeter. It consisted of an Alundum tube, *A*, 1-in. in inside diameter and 18 in. long, having a Chromel winding and surrounded by insulation. The upper end of the furnace tube was stoppered by a fired-talc plug, *E*, 2½ in. long. Auxiliary heating elements, *B*, covered a 3-in. length at each end of the furnace core. Proper apportioning of power to these end-heaters resulted in a more nearly isothermal environment within the furnace. The supplying of power to the upper end-heater was guided by the indications of a thermocouple whose principal junction was located in the upper part of the furnace tube. As there could be no obstruction to the fall of the capsule, the temperature could not be observed within the lower part of the furnace tube. The power required by the lower end-heater at various temperatures was determined by separate experiments in which a thermocouple junction was located in the lower part of the furnace tube. This junction was then removed. Tests made at temperatures up to 1,000° C with thermocouple junctions located at various points within the furnace indicated that under optimum conditions, gradients of only a few

[2] Figures in brackets indicate the literature references at the end of this paper.

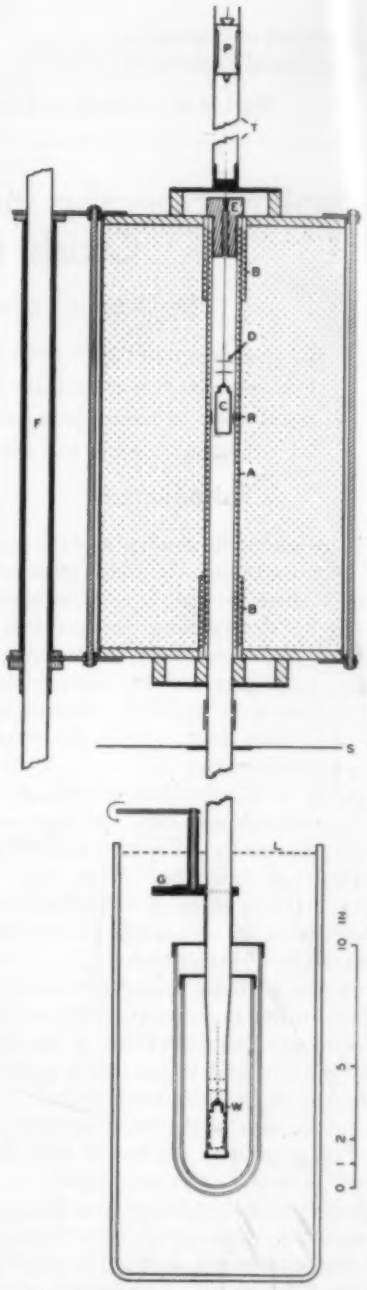

FIGURE 1.—*Schematic diagram of high-temperature enthalpy apparatus.*

A, Main heating element; *B*, end-heaters wound on short lengths of Alundum tube; *C*, capsule; *D*, shields; *E*, fired-talc plug; *F*, pipe supporting the furnace; *G*, gate mechanism; *L*, level of ice bath; *P*, plunger; *R*, silver ring; *S*, shield to protect ice bath from furnace radiation; *T*, tube 34 in. long; *W*, calorimeter well. Dotted figure shows position of capsule after fall. Details of ice calorimeter are omitted.

tenths of a degree an inch still existed in that region where the sample would be suspended. Power for the furnace was supplied through a constant-voltage transformer and was regulated manually.

The sample was contained in a Nichrome-5 capsule (fig. 2) having a screw cap of the same metal and a gold gasket for sealing. The capsule had a mass of 8.6 g (capacity of 7 ml) and was assembled by welding the bottom to the machined upper part at *A*. The gold gasket, *G*, was 0.3 mm thick. The capsule was filled with helium before sealing. A new gasket was used each time the capsule was to be sealed. The capsule (*C*, fig. 1)

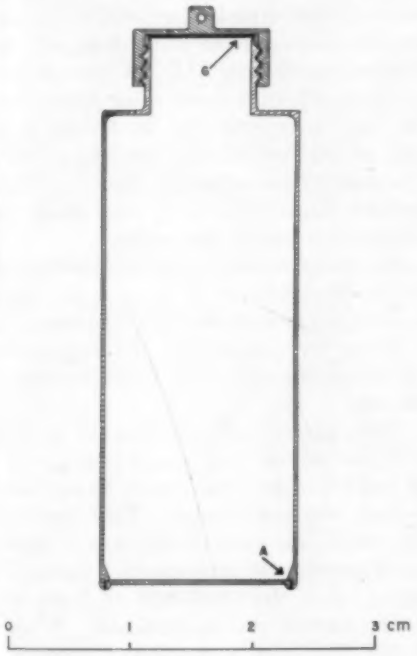

FIGURE 2.—*Capsule.*

A, Weld; *G*, gold gasket.

was suspended about midway in the furnace by a No. 32 B & S Chromel wire, the upper end of which was attached to a plunger, *P*, in a long vertical tube, *T*, situated on top of the furnace. The provision for releasing the system of capsule, wire, and plunger in practically free fall and slowing its drop by means of an air cushion once the capsule has entered the calorimeter was similar to that devised by Southard [2].

The function of the gate, *G*, was to intercept radiation down the well to the calorimeter. Its effectiveness is indicated by the fact that there was no observable difference in the calorimeter heat-leak rate with the furnace in place at 900° C or with it swung aside. The gate was held open for 2 seconds during each drop. A negligible amount of heat entered the calorimeter during this interval (about 0.1 cal with the furnace at 700° C) and would in any case have been accounted for in the blank experiments. Figure 3 shows how the gate carries the suspension wire against the wall of the calorimeter well in closing. This provides for intercepting any heat conducted along the suspension wire from the furnace.

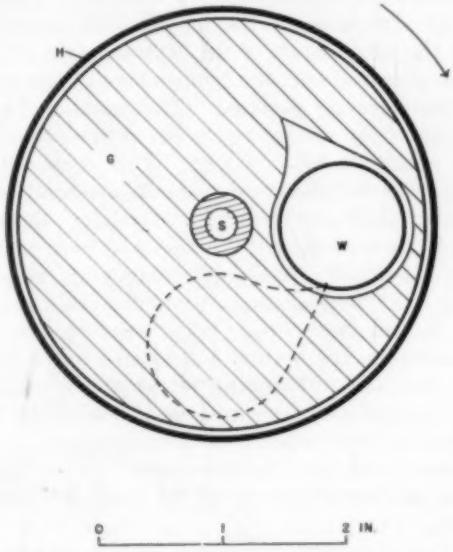

FIGURE 3.—*Calorimeter gate in open position viewed from above.*

G, Gate; *H*, housing; *S*, spindle; *W*, calorimeter well. Dotted line shows position of hole in gate after gate has been closed by rotation in direction of the arrow.

The temperature of the capsule and contents was measured by a platinum : platinum–10-percent rhodium thermocouple, whose principal junction was fused into a silver ring (*R*, fig. 1) consisting of a section of silver tube 12 mm long with a wall thickness of 0.5 mm. This ring fitted tightly within the Alundum furnace core and was located in such a way that the capsule would be within it when suspended in the furnace. Its purpose was (1) to provide for a rigid attachment

of the thermocouple junction that would not be easily dislocated by shock or thermal expansion, (2) by means of its high-thermal conductivity to provide some integration of the temperature around the furnace wall, and (3) to attach the thermocouple junction thermally to the furnace wall, thus preventing the temperature of the junction from being affected by conduction of heat along its leads. The effect of such conduction had been noted as a response of the thermocouple to variations in the temperature of that part of the furnace through which the leads pass. The effect was eliminated by installation of the silver ring.

The existence of temperature gradients in the furnace, together with the fact that the capsule when in the furnace presents a small solid angle to a cold surface below the furnace exit, suggested that the temperature of the capsule might not be quite identical with the temperature of the nearby thermocouple junction. The method of calibration of the thermocouple was such as to offset this effect, at least in part. This consisted in comparing the thermocouple with a second platinum : platinum–10-percent rhodium thermocouple whose principal junction had been placed within a dummy capsule approximating in size, shape, and thermal conductivity the real capsule, and the dummy capsule being inserted into the furnace from the bottom and located in the position that the real capsule would occupy in use. This second thermocouple was certified at the Bureau by comparison with a standard platinum: platinum rhodium thermocouple. In addition, it was calibrated directly at the steam and sulfur points.

All electromotive-force readings were made with a Wolff thermocouple potentiometer, the calibration of which was checked during the measurements. Although the emf of the thermocouple could be measured to within 0.1 μv (0.01°) and the furnace could be held constant to within a few hundredths of a degree, the measurement of temperature of the sample was probably not accurate to better than one-tenth degree up to 500° C. and several tenths at 900° C.

In addition to the measurement of the temperature in the furnace, it was necessary to allow sufficient time for the capsule and its contents to come to effective equilibrium with the furnace. This time was estimated early in the series of experiments. With simplifying assumptions, it may be shown that

$$\log_{10}\left[\frac{Q_0-Q}{Q_0}\right]=-\frac{t}{K},$$

where Q_0 is the heat evolved in any experiment in which the capsule has been in the furnace long enough before dropping to reach effective equilibrium, and Q is the heat evolved with a shorter time, t, in the furnace, the latter being held at constant temperature. The constant, K, which is evaluated by two such experiments, is equal to the time required for the temperature difference between capsule and furnace to be reduced by a factor of one-tenth. In the blank experiments, the capsule was held in the furnace at least 20 minutes before being dropped, whereas in the experiments with Al_2O_3, at least 45 minutes was allowed. In most cases, these times exceeded $4K$, so that any error due to failure to reach thermal equilibrium should have been less than 0.01 percent. In addition, occasional longer experiments (noted in table 1) were made with no consistent difference in the results.[2]

In addition to measuring the temperature of the sample in the furnace, it is also necessary to account for any loss of heat from the sample (a) in falling from the furnace to the calorimeter or (b) up the calorimeter well, while cooling in the calorimeter.

(a) Calculations indicate that in a drop at 1,000° C, the capsule may lose as much as 30 or 40 cal by radiation and convection to surroundings other than the calorimeter. This loss will be slightly less in the case of the empty capsule as compared to capsule plus sample, the difference depending upon the coefficient of heat transfer within the capsule and its contents. It has been calculated that, for a sample of average heat capacity, the above-mentioned difference will not exceed about 1 cal or about 0.05 percent of enthalpy of the sample and probably is less than 0.01 percent in experiments below 1,000° C. An additional error is possible if the rate of fall is not reproducible. The velocity of the capsule at a point just below the furnace exit (near S, fig. 1)

[2] It was also necessary to allow sufficient time after the drop for the capsule and contents to come to the temperature of the ice calorimeter. In this case, however, it was possible to observe directly in each experiment the time necessary to come to equilibrium. This time was on the average 26 minutes for the empty capsule and 66 minutes for the experiments with the Al_2O_3. These times included, of course, the time for the calorimeter itself to come to equilibrium.

TABLE 1.—*Results of individual experiments*

Blank experiments				Sample plus capsule			
Temperature	Date	Mass of mercury [a]	Deviation from mean	Temperature	Date	Mass of mercury [a]	Deviation from mean
°C		g	g	°C		g	g
50.3	Nov. 23, 1945	[d] 0.7043	−0.0004	50.3	Apr. 29, 1946	[b, d] 1.8646	0.0009
		.7035	−.0012			1.8629	−.0008
		.7064	.0017			1.8640	.0003
	Mean	0.7047			Mean	1.8637	
110.5	Nov. 26, 1945	[d] 1.5739	.0014	110.5	May 1, 1946	[d] 4.2945	−.0005
		1.5730	−.0015			4.2947	−.0003
		1.5747	.0002			4.2958	.0008
	Mean	1.5745			Mean	4.2950	
200.7	Nov. 23, 1945	2.9331	−.0046	200.7	Apr. 30, 1946	[d] 8.2733	.0008
		2.9382	.0006			8.2716	−.0009
		2.9395	.0018			8.2725	.0000
		2.9425	.0048		Mean	8.2725	
	Nov. 28, 1945	[d] 2.9369	−.0008				
		2.9383	.0006				
		2.9354	−.0023				
	Mean	2.9377					
300.9	Nov. 26, 1945	4.5078	−.0007	300.9	May 2, 1946	[b] 12.9940	.0024
		[b] 4.5085	.0000			12.9876	−.0040
		4.5093	.0008			12.9939	.0023
	Mean	4.5085			Mean	12.9916	
426.7	Nov. 27, 1945	[d] 6.5521	−.0014	426.7	Apr. 26, 1946	[d] 19.2351	−.0019
		6.5532	−.0003			19.2348	−.0022
		6.5552	.0017			19.2411	.0041
	Mean	6.5535			Mean	19.2370	
579.0	Nov. 27, 1945	9.1462	.0012	579.0	Apr. 25, 1946	27.1301	.0022
		9.1438	−.0012		May 3, 1946	27.1257	−.0022
		9.1451	.0001		May 6, 1945	[d] 27.1280	.0001
	Mean	9.1450			Mean	27.1279	
723.8	Nov. 21, 1945	[b] 11.8546	.0061	723.8	Apr. 25, 1946	[d] 35.0452	−.0095
		11.8485	.0000		May 3, 1946	35.0531	−.0016
		11.8459	−.0026		May 6, 1946	35.0641	.0094
	May 15, 1946	[c] 11.8346	−.0139		May 9, 1946	[c] 35.0234	−.0313
		11.8502	.0017			35.0480	−.0067
		11.8470	−.0015		May 10, 1946	35.0588	.0041
		11.8469	−.0016			[c] 35.0588	.0041
	Mean	11.8485			Mean	35.0547	
826.0	May 15, 1946	[d] 13.8146	−.0040	826.0	May 7, 1946	40.7804	−.0028
	May 16, 1946	13.8153	−.0033			40.7812	−.0020
		[d] 13.8258	.0072		May 13, 1946	40.7860	.0048
	Mean	13.8186			Mean	40.7832	
898.7	May 16, 1946	[d] 15.2381	−.0006	898.7	May 8, 1946	44.8931	.0035
		15.2359	−.0028			44.8818	−.0078
		[d] 15.2421	.0034		May 13, 1946	44.8940	.0044
	Mean	15.2387			Mean	44.8896	

[a] Corrected for buoyancy.
[b] These experiments were weighted slightly less because of unsteady heat leak.
[c] Experiments discarded on suspicion of moisture in calorimeter well.
[d] Time in furnace on these experiments was at least 20% more than on those of same group not so marked.
[e] CO_2 flow-rate in calorimeter was about three times as great as usual.

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was determined by suspending a magnet below the capsule and measuring with a cathode ray oscilloscope the emf produced in a coil through which the magnet fell when the plunger was released. The velocity was found to be reproducible within the uncertainty of the measurement, which was about 2 percent. Also, it was within 2 percent of the velocity of free fall of the magnet in air. During the heat measurements, the weight of the falling system was kept constant, regardless of the weight of sample, by means of small weights that could be added to or removed from the plunger.

(b) Approximate calculations indicated that the loss of heat up the calorimeter well by radiation and conduction from the hot capsule after its fall was quite small for temperatures up to 1,000° C. However, the convection loss remained unknown, and for the purpose of minimizing it as well as the other upward losses, there was employed a system of thin, horizontal platinum shields (D, fig. 1) of the same diameter as the capsule and spaced about ½ in. apart on the suspension wire immediately above the capsule. The effectiveness of the shields was tested by drop experiments at 725°, in which the number of shields was varied while maintaining the heat capacity of the system constant. The heat evolved was about 2,000 cal for each experiment. In going by steps from one to four shields, the total range of variation in the heat transferred to the calorimeter in each experiment was 0.7 cal, the variation being largely random. With no shields the heat transferred to the calorimeter was less by 5 cal. Thus one shield appeared to be adequate for confining the convection. In the experiments with Al_2O_3, two shields were employed.

III. Results

The results of 31 experiments with the sample and 35 blank experiments are given in table 1. The blank experiments were made at the same series of temperatures as the experiments with sample. In this table are listed the masses of mercury taken into the ice calorimeter in the respective experiments. Two classes of corrections have been applied to these masses. These corrections are small and therefore are not listed separately. The first class comprises corrections for slight deviations from ideal calorimetric behavior, that is, for heat leak and the change in position of the mercury meniscus between the beginning and end of an experiment. These corrections were roughly independent of the magnitude of the heat involved in an experiment, and each kind averaged only about 0.002 g of mercury (equivalent to about 0.1 cal). The second class of corrections accounted for small differences in the amount of gas and gold contained in the capsule in the experiments with the sample as compared with the blank experiments and also accounted for small variations in capsule weight resulting from slow surface oxidation of the Nichrome wire at temperatures above 800°. These corrections, when lumped together, were approximately proportional to the amount of heat in an experiment and averaged about 0.04 percent of the net mercury intake (that due to sample alone).

In table 2 the conversion of experimental data to enthalpy of Al_2O_3 is completed by using 64.638 cal/g of mercury (1 cal=4.1833 int. j) for the "apparent" calibration factor of the ice calorimeter [1]. An arbitrary enthalpy-temperature curve was drawn through the data of table 2, values were read off at even temperature intervals, and the results were smoothed. The deviations of the observed enthalpies from the smoothed values before rounding off the latter are given in the last column of table 2.

TABLE 2.—*Computation of enthalpy—Comparison with smoothed values*

Temperature, t	Net mass of mercury [a]	Enthalpy [b] $H_{obs.}]_0^t$	Enthalpy observed minus smoothed
°C	g	cal. g^{-1}	Percent
0	0	0	
50.3	1.1590	9.317	−0.03
110.5	2.7205	21.870	.02
200.7	5.3348	42.886	.11
300.9	8.4831	68.195	−.05
426.7	12.6835	101.962	−.02
579.0	17.9829	144.564	−.05
723.8	23.2062	186.553	.01
826.0	26.9646	216.767	.03
898.7	29.6509	238.362	.00

[a] From table 1: Means from column 7 minus means from column 3.

[b] Mass of sample=8.0406 g; "apparent" calibration factor of ice calorimeter=64.638 defined calories per gram of mercury.

Values of specific heat, $C_p=(\partial H/\partial T)_p$, were obtained from the smoothed enthalpy data by the method of Rutledge [3]. The entropy (re-

ferred to 0° C), $S]_0^t = \int_0^t (C_p/T)dt$, was calculated by using Simpson's rule. The smoothed values of enthalpy and the derived quantities are given in table 3.

TABLE 3.—*Enthalpy, specific heat, and entropy of Al_2O_3 at even temperature intervals*

[1 cal=4.1833 int. J; 0° C=273.16° K]

Temperature	$H]_0^t$	C_p	$S]_0^t$
°C	Cal g⁻¹	Cal g⁻¹deg⁻¹C	Cal g⁻¹deg⁻¹K
0	0	0.1731	0
20	3.86	.1830	0.01259
40	7.32	.1922	.02498
60	11.25	.2007	.03714
80	15.34	.2085	.04906
100	19.56	.2157	.06074
120	23.96	.2224	.07218
140	28.47	.2285	.08337
160	33.10	.2341	.09431
180	37.84	.2392	.10499
200	42.67	.2438	.11542
220	47.59	.2480	.12560
240	52.59	.2518	.13554
260	57.66	.2552	.14524
280	62.80	.2583	.15470
300	68.00	.2611	.16393
320	73.25	.2637	.17293
340	78.54	.2660	.18171
360	83.88	.2681	.19028
380	89.26	.2701	.19865
400	94.68	.2719	.20682
420	100.14	.2736	.21480
440	105.63	.2753	.22260
460	111.15	.2769	.23023
480	116.70	.2784	.23770
500	122.28	.2799	.24502
520	127.89	.2813	.25219
540	133.53	.2827	.25922
560	139.20	.2840	.26611
580	144.90	.2853	.27287
600	150.62	.2865	.27950
620	156.36	.2877	.28600
640	162.13	.2888	.29238
660	167.92	.2899	.29865
680	173.73	.2909	.30481
700	179.56	.2919	.31086
720	185.41	.2928	.31681
740	191.28	.2937	.32266
760	197.16	.2945	.32841
780	203.06	.2953	.33406
800	208.97	.2960	.33962
820	214.90	.2967	.34509
840	220.84	.2974	.35048
860	226.80	.2981	.35579
880	232.77	.2988	.36102
900	238.75	.2995	.36617

IV. Discussion of Results

1. Reliability

An index to the reproducibility, or "precision", of the enthalpy measurements is given by the deviations from the mean (table 1). The average deviation of this type was 0.015 percent in the experiments with the sample. Another index is given by the deviations of the mean observed values of enthalpy from the "smoothed" values (table 2). The average deviation of this type was about 0.035 percent. In addition to the accidental errors there must be considered the possibility of systematic errors. For example, the calibration factor of the calorimeter may be in error by 0.02 percent [1]. The possibility of error in the measurement of temperature has already been discussed as well as the error attached to the heat loss in dropping. From consideration of these and other errors, the authors believe that the smoothed values of enthalpy given in table 3 do not differ by more than 0.2 percent from the true values, except below 100° C, where the relative sensitivity of the apparatus and method is less. This estimate of error is supported by measurements of the enthalpy of liquid water [4] at 254° C using the same apparatus, with the exception of the capsule. The results were within 0.04 percent of what may be considered an accepted value [4].

In addition to the error in the determination of enthalpy, an error of about the same magnitude has been introduced in determining the derived quantities of specific heat and entropy. These quantities also possess an increased uncertainty above 850° C due to the difficulty of determining the derivative of a function near its end.

2. Comparison with Other Investigations

The specific heats near 0° C could have been adjusted so as to conform more nearly to the low-temperature measurements of Parks and Kelley [5] and Simon and Swain [6], which extend up to near 20° C. However, the results in table 3 are already within, at the most, 0.9 percent and on the average 0.5 percent of the five determinations of the above authors in the range of overlap. As the deviations are not greater than the estimated

[4] These measurements will be described in more detail in a paper on *p*-xylene which will follow in another journal.

error of any of the investigators concerned, and as the present results fall below those of Parks and Kelley and above that of Simon and Swain, no attempt was made at any adjustment.

There have been several high-temperature measurements on Al_2O_3. For comparison, these results have been placed on the basis employed in this paper, that is, mean specific heats or enthalpies between high temperatures and room temperature have been converted to enthalpies referred to 0° C by using data in table 3. These adjustments are small in all cases and are not subject to sufficient uncertainty to materially affect the comparisons among different authors.

Figure 4 shows the derived specific heats from

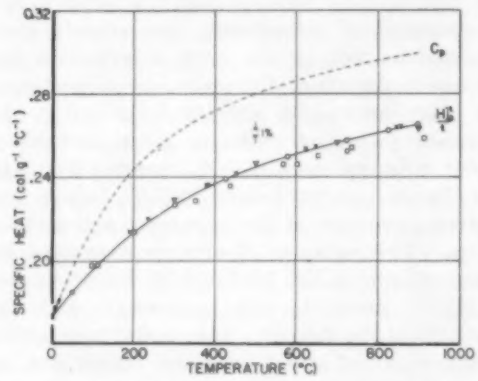

FIGURE 4.—*Comparison of mean and true specific heats of* Al_2O_3 *with those from some other investigations.*

C_p, ..., NBS (derived); ●, Parks and Kelley; ■, Simon and Swain; $\frac{H_0^t}{t}$, ——, NBS (smoothed); ○, NBS (observed); ×, Shomate and Naylor; ▽, von Gronow and Schwiete; □, Roth and Bertram.

table 3 compared with the observed specific heats of Parks and Kelley, and Simon and Swain. The mean specific heat, H_0^t/t, is also plotted showing results of selected investigators for comparison. Use of the quantity H_0^t/t rather than H_0^t serves better to show up differences between investigators as well as irregularities in the work of any one investigator. The results of von Gronow and Schwiete [8] and Shomate and Naylor [9] are within 1 percent of those of this investigation, whereas the results of Roth and Bertram [10] are within 2 percent, with one exception. Observed data of the above authors were used in plotting figure 4, except for von Gronow and Schwiete, who published only smoothed results.

No weight is attached to the work of Cohn [11], Kolosovski and Skoulski [12], Newman and Brown [7], Miehr, Immke, and Kratzert [13], Wilkes [14], Esser, Averdieck, and Grass [15], Lyashenko [16], Auzhbikovich [17], Cherbov and Chernyak [18], or earlier investigators because of obvious defects in experimental methods and/or sample. The results of the above authors differ by several percent on the average from those of this investigation, being lower for the most part, except from 100° to 200° C, where they cluster about the results of this investigation.

V. Conclusions

The results of the present investigation indicate that Al_2O_3 in the form of synthetic sapphire (corundum) is admirably suited to serve as a standard of heat capacity in the range 0° to 900° C. There is no apparent reason why it should not serve equally well in the range 0° K to 0° C, and from 900° C up to at least 1,600° C.

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Transmission Measurements With The Beckman Quartz Spectrophotometer

By Kasson S. Gibson and Margaret M. Balcom

The Beckman quartz photoelectric spectrophotometer, covering the wavelength range from about 200 to 1,200 millimicrons, is proving of great utility in spectral transmission and absorption measurements. Essential features of the instrument are described, including a constant-temperature enclosure (for samples) designed and constructed at the Bureau. Various instrumental characteristics are noted and possible errors discussed, particularly those that may be present in the measurement of polarizing samples. Wavelength calibrations are shown for two instruments. A detailed over-all check of the reliability of data obtained on the Beckman spectrophotometer by means of glass standards of spectral transmittance shows it to give results over the wavelength range from 390 to 750 millimicrons fully as reliable as those obtained with other spectrophotometers, if indicated precautions are taken.

I. Introduction

In a standardization and testing institution such as the National Bureau of Standards it is essential that every means be taken to insure accuracy of results. It is further desirable that many different methods and instruments be available to handle the wide variety of testing submitted.

This is true in spectrophotometry as in other fields. Spectrophotometers are subject to many annoying and hard-to-detect errors. One can have a good instrument, make a careful wavelength calibration, reduce stray light to negligible proportions, reduce the slit widths or use homogeneous radiant energy, test the photometric scale, and control the temperature of the instrument or the sample. In this and other ways he may believe that the results obtainable over the better part of the appropriate wavelength range are highly accurate. He may also do this with other instruments of different type, covering the wavelength range in which he is interested.

He may then carefully measure the spectral transmittance [1] of a glass on each instrument but find that the results do not agree to the expected extent. He may or may not have the time or otherwise be able to eliminate the discrepancy. For this reason it is advisable to have several different types of instruments on hand, especially if spectrophotometric standards are being issued to other laboratories to check the performance of their instruments, or if effort is being made to determine with the greatest certainty the true values of transmittance at the specified wavelengths.

With respect to the wide variety of work submitted, transmission values may range from unity down to a few hundredths of 1 percent (for example, welding glasses or filters for viewing searchlights), and these values may be desired to two or three significant figures. Also, the wavelength ranges of all spectrophotometers are limited, and values obtained near the ends of these ranges are usually of lowered reliability. Furthermore, most spectrophotometers are de-

[1] The terms *spectral transmittance* (T) and *spectral transmittancy* (T_τ) are used as defined in the Optical Society of America Colorimetry Committee Report (J. Opt. Soc. Am. **34**, 183; 1944). *Spectral transmittance* (p. 184 and 188) is thus the ratio of transmitted to incident radiant flux, evaluated for a particular wavelength of incident energy. In the present paper the term is often abbreviated simply to *transmittance*. *Spectral transmittancy* (p. 189) is the ratio of the transmittance of a solution to that of the solvent in equivalent thickness, again evaluated for a particular wavelength. It can be measured if the solution and solvent are placed in identical absorption cells.

Consistent with the above, the word *transmission* has been discontinued as a specific term, along with many other words ending in *ion*. As an adjective, however, the word is often useful when it is desired not to be specific. For example, in the present paper, the word *transmission* is used where the statement being made would apply both to the measurement of transmittance and to the measurement of transmittancy.

signed primarily for special purposes and will handle adequately only a limited variety of testing.

For reasons such as these, the Photometry and Colorimetry Section of the National Bureau of Standards maintains several types of spectrophotometers that have been developed by the Bureau or purchased over a period of years. The development or operation of these has been described in numerous publications listed in Bureau Letter Circulars LC398, 628, and 789, and reference to some of these instruments is made later in the paper.

Two of the Beckman quartz spectrophotometers have been obtained by the Photometry and Colorimetry Section, one in 1943 and one in 1945. These were not obtained for the purpose of "testing" the instruments but to facilitate the large amount of standardization and testing work of the Section, especially during the war periods. A complete study of the instruments therefore has not been made, but sufficient information on their calibration and operation has been obtained to be of interest and value to others, as was true earlier with the General Electric recording spectrophotometer.[2]

The scope of the present paper is limited mostly to transmission measurements, although much of the information obtained is equally useful in reflection work. Furthermore, only the optics of the measurements are considered, little study having been made of the electric circuits of the Beckman spectrophotometer. A few of the points noted were briefly considered in a recent publication.[3]

II. Description and Operation of the Instrument

The Beckman spectrophotometer has been discussed in some detail in a paper by Cary and Beckman.[4] In that paper questions of design, stray radiant energy, phototube sensitivity, electric circuits, and slit widths are considered and illustrated. Figure 1 of the present paper is a reproduction of figure 3 of the paper by Cary and Beckman.

[2] Kasson S. Gibson and Harry J. Keegan, Calibration and operation of the General Electric recording spectrophotometer of the National Bureau of Standards, J. Opt. Soc. Am. **28**, 372 (1938).

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Radiant energy from an incandescent lamp or other illuminant, *A*, is focused on the slit, *D*, by means of the concave mirror, *B*, and the plane mirror, *C*. The beam entering the slit is collimated by mirror *E* and passes through the quartz prism to the reflecting surface, *F*. After reflection at *F* the beam returns along nearly the same path to the same slit, *D*, where it emerges slightly above the entrance beam and mirror *C*. After passage through the sample or sample compartment, *G*, the beam is incident on the phototube, *H*.

FIGURE 1.—*Optics of the Beckman spectrophotometer.*
This is a reproduction of figure 3 of the paper by Cary and Beckman, J. Opt. Soc. Am. **31**, 682 (1941).

Two phototubes are supplied installed in the instrument, either of which may be inserted in the beam at will. One is a "cesium oxide" phototube ("red sensitive") for use primarily in the range from 620 to 1,200 mμ. The other is a special "cesium antimony" phototube ("blue sensitive") for use primarily below 620 mμ. If incandescent lamp and common glass phototube are used, this range terminates at about 320 mμ. If the tube has an envelope of Corning 9740 glass, and if a hydrogen lamp with a window of the same type of glass is used as source (all supplied with the instrument when desired), the range extends to about 210 mμ.

The photometric scale is based on electrical rather than optical principles. The photoelectric current from the irradiated cell produces across the phototube load resistor a voltage drop which is balanced by a potentiometer. While this null setting is being made any imbalance is amplified electronically and is indicated by a milliammeter on the instrument. Accuracy of the photometric scale depends, among other things, on conformity of the phototube load resister to Ohm's law, and on the linearity of the irradiation-current relationship. As vacuum phototubes are used, the relation should hold closely. It is understood that linearity is still further assured by the use of a frame-type anode in the phototubes.

In general, three readings are necessary to make a transmission determination at any wavelength,

(1) the zero reading, in which the beam is blocked from the phototube by an "off" shutter, and the galvanometer is brought to balance by a "dark current" adjustor, (2) the 100-percent reading, in which the beam falls on the phototube after passing through the transmission standard (blank beam, solvent cell, or standard glass), and the milliammeter is brought to balance by adjusting the slit width or the "sensitivity" adjustor, and (3) the transmission reading, in which the unknown or test sample is placed in the beam and the galvanometer, is brought to balance by turning the potentiometer dial carrying the "transmission" or "density" [5] scale. The 100-percent reading may be made either by setting the dial to 100.0 or, more conveniently, by setting a selector switch to "check". This switch is then set to "1" for the the transmission reading, or to ".1" if it is desired to read transmission values between 0.0000 and 0.1000 on a "$\times 10$" scale. Unless the transmission values are low (below 0.10), the zero reading does not usually have to be checked at every wavelength.

The instrument is designed primarily to measure the transmittancy, T_s (or $-\log_{10} T_s$) of solutions relative to solvent in a 1-cm thickness, and a holder is supplied for carrying the 1-cm cells furnished with the instrument, as well as shorter cells, which are also available. To measure the transmittance of glasses, it was necessary to construct a special holder that would fit into the shifting platform. The glass can thus be readily moved in and out of the beam. Samples up to about 2 inches square can be accommodated.

To handle solutions up to 10 cm in thickness the manufacturers supply an alternative sample chamber which may be placed between the instrument slit and the phototube compartment. They also supply absorption cells 2, 5, and 10 cm in length with adjustable holder. This auxiliary equipment was purchased with the first Beckman spectrophotometer, but for reasons of convenience, the carrier has been replaced by a constant-temperature enclosure designed in the Photometry and Colorimetry Section, which will accommodate the absorption cells used with the Bureau's König-Martens and Gibson spectrophotometers.

[5] The words "transmission" and "density" are engraved on the dial on which the scales are carried. By *density*, in this case, is meant the negative logarithm of transmittance or transmittancy.

1. Constant-Temperature Enclosure

This constant-temperature enclosure is somewhat similar to those used on the above spectrophotometers. The outside dimensions were necessarily smaller, however, as it had to fit light-tight into the sample chamber supplied with the Beckman instrument.

Figure 2 shows this enclosure along with various other accessories related to the instrument or the measurements. The temperature of the holder, *A*, is kept constant at 25° C or other desired temperature by means of water pumped through

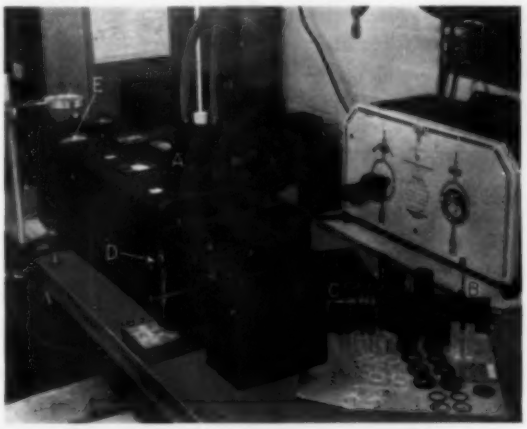


FIGURE 2.—*Beckman spectrophotometer and various auxiliary equipment as installed and used in the Photometry and Colorimetry Section of the National Bureau of Standards (see text for explanation).*

from a constant-temperature bath. The temperature of the water in the holder is indicated by the thermometer shown, the bulb of which is placed inside between the two cell compartments.

The absorption cell parts are shown beside the instrument. These cells are 1, 2, 4, or 10 cm in length. They have been described in detail in previous publications.[6] They consist of glass tubes on the inside, with separate glass or quartz end plates held on by the brass caps. The cells are thus easily taken apart for cleaning.

The diameter of the openings in the constant-temperature enclosure is about 30 mm, just large enough to hold the absorption cells shown and also

[6] K. S. Gibson, H. J. McNicholas, E. P. T. Tyndall, M. K. Frehafer, W. E. Mathewson, The spectral transmissive properties of dyes. I. Seven permitted food dyes in the visible, ultra-violet, and near infra-red, BS Sci. Pap. **18**, 121 (1922) S440. Also described in RP30 (see footnote 12).

the glass standards of spectral transmittance which the National Bureau of Standards issues. Other samples, such as 2-inch squares of glass or plastic, can be mounted on the outside of the holder resting on the platform and held in place by a spring finger.

This means of temperature control is considered adequate for the purpose, which is primarily to hold the samples at some specified temperature within room-temperature range. In Washington, D. C. these room temperatures may vary from less than 20° C in the winter to about 35° C in the summer, and such variations may have important effects on transmission values. An additional reason for the temperature control is that the lamp sources on the Beckman spectrophotometer are closely adjacent to the sample compartment, and without the control, the whole enclosure (with samples) slowly heats up during extended measurements.

Although this means of temperature control is primarily for maintenance at 25° C, it is also considered adequate for maintaining the absorption cells and 30-mm glass standards at temperatures from about 25° up to 55° C, and has often been so used.

Certain other points of interest may be noted in figure 2. At *B* is the holder for glass samples to which reference has already been made, used when temperature control of the sample is unnecessary. At *C* is the four-compartment solution-cell holder supplied with the instrument. At *D* is the slide carrying the stray-energy filter, supplied with the instrument.

At *E* is an auxiliary indicator line which has been added above the wavelength scale of the instrument. The use of a single indicator line, as installed in the instrument, results in parallax and consequent uncertainties of wave length setting larger than desired. A slide-rule indicator glass fits nicely into the space, and was cemented onto the instrument glass with the black line up. The two fine lines thus presented greatly increase the precision of wave-length settings.

2. Multiple Reflections

Certain other points regarding the instrument and its operation may be noted. On the 1943 instrument both slits were covered with plane quartz plates to keep out dust and fumes. However, the normal divergence of the exit beam prevented accurate measurements with 10-cm cells, the beam hitting the sides of the cell near the far end. To remedy this the quartz plate over the exit slit was changed to a lens of 30-cm focal length, which rendered the beam more or less "parallel" and made it possible to use cell lengths up to 10 cm. On the 1945 instrument, the quartz plate over the exit slit had been replaced by this type of lens when received.

On both instruments this lens has been placed in the sliding piece carrying the stray-energy filter, so that it can be moved in or out at will, and no plate or lens has been left over the exit slit. This is to avoid the slight multiple-reflection error obtained with the quartz plate or lens in use when a glass sample is measured relative to a blank beam. For a nonabsorbing glass sample of index 1.7, the error in T, by measurement, amounts to about 1 percent, the value obtained being too high. When solutions are measured relative to solvents in similar cells, or when one glass is measured relative to another, this effect is usually of negligible importance. Further troubles originating in the quartz plates are discussed below.

3. Stray Spectral Energy

Stray light can readily be perceived by looking directly into the exit slit of the instrument at a region of low luminosity—for example, below 450 or above 700 mμ. Likewise, in the spectral regions to which the phototubes are relatively insensitive, stray energy from the rest of the spectrum may be present in important amounts. It should be noted that, with the usual type of cesium oxide phototube, the response obtained from 1,200 to 2,000 mμ on the Beckman spectrophotometer is produced almost entirely by stray energy. Enormous errors may be obtained if the instrument is used at scale settings nominally in this region.

One stray-energy filter is supplied with each instrument, as already indicated. This is a dense purple glass, transmitting the ultraviolet freely and absorbing the visible strongly, and, as recommended, should always be used when measurements with the incandescent source are being made below 400 mμ. A similar (blue) filter for the region from 400 to 500 mμ is advantageous for some work. In this region, erroneous values of transmittance from 0.001 to 0.005 may be obtained with nonfluorescent yellow selenium

glasses, whose true transmittance is known to be 0.000.

This example shows that the importance of stray energy depends not only on the spectral region but also on the type of glass or solution being measured. This is further mentioned below in connection with the measurements made on the cobalt-blue spectrophotometric standard. Additional slides have been purchased for holding stray-energy filters of varying type, which may be inserted at will in the instruments.

To avoid multiple-reflection errors, the stray-energy filter should be mounted with surfaces inclined somewhat to the plane of the sample being measured.

4. Measurement of Fluorescent Samples

In spectrophotometers where the radiant energy is dispersed before incidence upon the sample, an error of measurement may occur with fluorescent samples. For example, if energy of wavelength 550 mμ excites reddish fluorescence, this fluorescent energy is incident directly upon the phototube and adds to the photocurrent excited by the normally transmitted or reflected energy at 550 mμ. The magnitude of this error depends on the ratio of fluorescent to incident energy and on the relative sensitivity of the phototube to the incident and the fluorescent energy.

The error is apparently never very large in transmission measurements because the fluorescent energy is emitted throughout the whole spherical solid angle, and only a small fraction of it is incident upon the phototube. If of importance, the error can be reduced by placing the sample as far from the photocell as possible and by the use of selective filters transmitting the incident energy freely and absorbing the fluorescent energy strongly. The error is of much greater importance in the spectral reflection measurement of diffusing samples, because here the angle of the fluorescent energy accepted for measurement bears the same ratio to the full hemispherical angle as does the reflected spectral energy itself.

III. Other Instrumental Characteristics

A matter of interest and importance in the use of any spectrophotometer is the relative spectral response of the receptor and the spectral purity of the radiant energy transmitted by the exit slit under normal working conditions. The former is of importance in connection with study or elimination of errors resulting from stray energy, and the latter is of importance (along with other factors) in any consideration of the absolute accuracy of spectral-transmission measurements.

Information on both of these points is given in the paper by Cary and Beckman. In their figure 4 the relative photocurrents for nominal band widths of 3 mμ are illustrated, and in their figure 9 are given the minimum spectral band widths that permit scale readings to 0.1 percent. For the Bureau instruments it was desired to know the relative spectral response of each phototube when the slits are kept at a constant mechanical width and to determine the spectral band widths transmitted by the exit slit over the whole wavelength range under normal working conditions, this latter amounting to a check of Cary and Beckman's figure 9.

1. Spectral-Response Curves

The relative response curves were obtained for each phototube with the incandescent illuminant in normal operation. With the selector dial set at "1" the slits were adjusted to give a reading of 100.0 at the wavelength of maximum response for each cell. Readings on the photometric scale were then made at the various wavelengths through the spectrum, continual check (and slight adjustment if necessary) being made to keep all readings truly relative to 100.0 at the respective wavelengths of maximum response. When the relative response fell to about 10.0 the selector dial was changed to ".1", and the readings were made to one more decimal place. The results are shown in figure 3. Readings were taken at every 2 or 10 mμ, as there shown. The data for the blue-sensitive phototube were obtained with the 1943 instrument; those for the red-sensitive phototube with the 1945 instrument. Data obtained with different phototubes are of course somewhat different, but those shown are considered typical. It may be repeated that these data are for constant mechanical slit width and are not corrected for dispersion of the prism or other selectivity within the instrument or for energy distribution of source.

2. Polarization Effects

It may be noted that some of the curves of figure 3 are smooth and typical of the response curves ordinarily obtained with phototubes of these kinds with incandescent illuminant and prismatic dispersion. The other curves, however, are characterized by ripples superposed on the response curves. This is shown by curves 1 and 3 of figure 3.

The primary factor causing these ripples is the quartz plate over the entrance slit. This plate on both instruments was found to be cut with its faces parallel to the optic axis of the quartz crystal.[7] When such a plate is placed between polarizing elements and oriented so that its axis is not parallel with that of either of the polarizing elements, the spectrum contains a number of dark bands regularly spaced throughout. The conspicuousness of these bands depends on the degree of polarization of the polarizing elements and on the deviation of the optic axis of the quartz plate from the polarization planes of these elements, being greatest if at 45° to both of these planes.

The following explanation of the effect is given by R. W. Wood. When plane polarized light is passed through a doubly refracting crystal plate cut parallel to the axis, "it is resolved i two components vibrating at right angles each other which traverse the plate with differ velocities and consequently emerge with a pha difference depending on the thickness of the pl . . . Owing to dispersion the phase-differe of the emergent components depends not o on the thickness of the crystal plate but also on wavelength of the light, consequently if wh light is employed the state of polarization of transmitted light varies as we pass along spectrum, and if a plate of moderate thickness used and the light is passed through a Nicol a into a spectroscope, the spectrum will be fou to be furrowed by dark bands which repres the wavelengths quenched by the Nicol." [8]

In the present instance the polarizing elemen appear to be (1) the incandescent filament its (which may give up to 20-percent polarization modified possibly by elliptical polarization by t two mirrors, on one side of the quartz plate, a (2) the refracting surface of the dispersing pris on the other side.

[7] Determinations made by F. P. Phelps of the Bureau's Polarimetry Section, from whom helpful advice in this connection was received.

[8] Physical optics, 3d ed., p. 349 (The Macmillan Co., New York, N. 1934).

[9] A. G. Worthing, Deviation from Lambert's law and polarization of l emitted by incandescent tungsten, tantalum, and molybdenum and chan in the optical constants of tungsten with temperature, J. Opt. Soc. Am. 635 (1926).

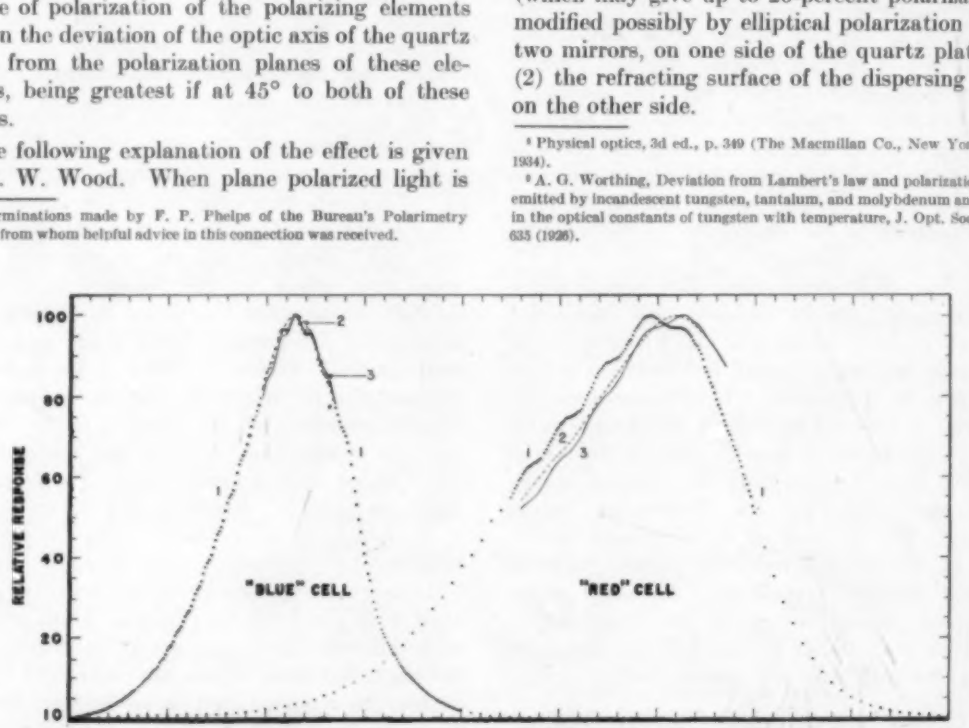


FIGURE 3.—*Spectral-response curves of phototubes in a Beckman spectrophotometer.*

These are as obtained, relative to 100.0 at the respective maxima, for constant mechanical slit widths and with no corrections for energy distributio of source, dispersion of spectrometer, or other factors affecting the selectivity. For explanation, see text.

The ripples in the sensitivity curves are not apparent if (1) the quartz plate is oriented with its axis at 0° or 90° to the polarizing plane of the dispersing prism, (2) the plate is removed from the instrument, (3) a quartz plate cut, perpendicular to the axis is used over the entrance slits, (4) a glass plate is used over the entrance slit. The quartz lens or plate in the upper beam (regardless of how cut) has no appreciable effect on the sensitivity curve at any orientation; in this case, the quartz is not between polarizing elements. The band effect can readily be seen if the quartz plate (faces cut parallel to optic axis) is taken out of the instrument and examined between polarizing elements with a hand spectroscope. One of the polarizing elements may be the sky or a bare tungsten filament. The filament of the incandescent source of the Beckman spectrophotometer is thus demonstrated to be giving off partially polarized light. The dispersing prism of the hand spectroscope is the second polarizing element. Of course, the effect is far more pronounced if the polarizing elements are two Polaroids or nicols.

With reference to figure 3, again, curves 1 were obtained soon after the receipt of the respective instruments. In both cases the entrance quartz plate had not been disturbed before the data were taken, and it would appear from the magnitudes of the ripples that each plate had been mounted with its axis approximately at 45° to the polarizing planes of the dispersing prism and lamp filament. The other curves of figure 3 were obtained later, curves 2 with the entrance quartz plate removed, curves 3 with it reinserted at the 45° position. It may be noted, incidentally, that curves 1 and 3 ("blue" cell), which check closely, were obtained with different phototubes; curves 2 and 3 ("red" cell), which show change of sensitivity, were obtained with the same phototube 14 months apart.

It was at first thought that the ripples shown in figure 3 were of no particular importance. However, when measurement of the spectral transmittance of polarizing materials was attempted, it was found that the ripples were caused by some polarization phenomena, and could no longer be ignored. The effect was accordingly investigated, as partially described above. It is unnecessary to consider all the data obtained, but it is worthwhile to point out some of the results obtained if due precautions are not taken.

For example, in figure 4, top, is shown (1) the "transmittance" curve obtained on a polarizing goggle inserted in the carrier of the Beckman spectrophotometer at random orientation[10] and with the entrance plate of the instrument at unknown orientation. From 570 to 600 mμ are shown also (2) the maximum and minimum values of "transmittance" obtained by turning the goggle in its own plane (90° apart), and (3) the corresponding values obtained on the Gibson photoelectric spectrophotometer (with Hilger constant-deviation glass prism). Similar ripples have been noted in the transmission curves of polarizing materials obtained by others with Beckman quartz spectrophotometers.

The effect was studied at some length by measuring the "transmittance" of a Polaroid sample, these measurements more or less paralleling in time those from which the sensitivity curves were obtained, as described above. Some of the data are presented in the lower half of figure 4.

In figure 4 *A*, the quartz plate over the entrance slit is placed with its optic axis at 45° to the slit, and no plate or lens is over the exit slit. The angles shown beside the five curves in *A* refer to various orientations of the polaroid. In the 0° position the electric vector of the radiant energy transmitted by the Polaroid is in the vertical plane parallel to the slits and the refracting faces of the dispersing prism. At +45° and −45° the Polaroid is turned at 45° from the 0° position. At +90° and −90° the Polaroid is turned at right angles from the 0° position.

In *B* and *C*, figure 4, the quartz entrance plate has been turned so that the optic axis is respectively horizontal and vertical, the angles on the graphs indicating the same respective orientations of the Polaroid as before. No plate or lens is over the exit slit.

In *D*, figure 4, the quartz entrance plate has been removed, and there is no plate or lens over the exit slit. For comparison are shown (the large crossed circles) the corresponding values obtained on the Gibson glass-prism spectrophotometer.

In *E*, figure 4, the quartz plate is still removed from the entrance slit but has been inserted over the exit slit at the 45° position. Data were also obtained with the quartz plate over the exit slit oriented at 0° and 90°. At 0° the curves obtained

[10] The shape and size of the sample did not permit of orientation at 45°.

were similar to the Beckman (small circle) curves of figure 4,*D*, with about the same total spread. At 90° the curves were similar to those of figure 4,*C*, but with a total spread of only 0.02.

The following comments may be made regarding the data of figures 3 and 4.

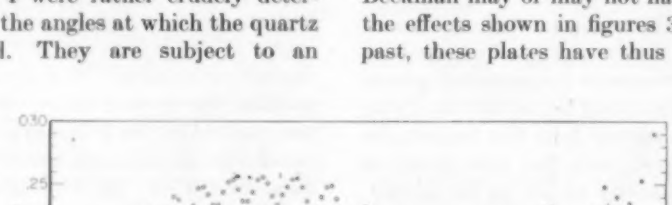
1. The conditions causing the ripples of figure 3 are the same as those causing the worst distortions, figure 4,*A*, during measurement of the transmittance of polarizing samples. It is probable that the entrance quartz plate was close to the 45° position when the data shown in the top half of figure 4 were obtained.

2. Complete elimination of the trouble is effected by removing both quartz plates (or plate and lens) over the entrance and exit slits, figures 3 and 4,*D*.

3. Residual effects not apparent in the sensitivity curves may be found (by means of the Polaroid) under other than 45° orientation of the entrance quartz plate (cut parallel to the optic axis). Such residual effects are shown in figures 4,*B* and *C*, and in other data not given. In this connection it should be pointed out that the angles indicated in figure 4 were rather crudely determined, particularly the angles at which the quartz plate was oriented. They are subject to an uncertainty of at least ±5°. Whether or not, for example, the "ripples" of figure 4,*B* and *C* would be eliminated by more exact 0° and 90° positioning was not investigated.

4. With both quartz plates removed the errors possible in the measurement of a polarizing sample at random orientation appear much less than on a glass-prism instrument. Note in figure 4,*D* the total spread of about 0.02 on the Beckman as contrasted with the spread of about 0.11 on the Gibson instrument. This is undoubtedly largely due to difference in the angle at which the radiant energy enters and leaves the respective quartz and glass prisms at 530 mμ on the two instruments.

Many of these results were shown to Mr. Cary (see footnote 4) in November 1946, who indicated that the entrance plates and the exit lens or plate were cut from wastage material remaining from construction of the quartz dispersing prisms and that the optic axis in these plates may be parallel or perpendicular to the faces or at angles in between. Accordingly, other users of the Beckman may or may not have been bothered by the effects shown in figures 3 and 4. As, in the past, these plates have thus been cut at various



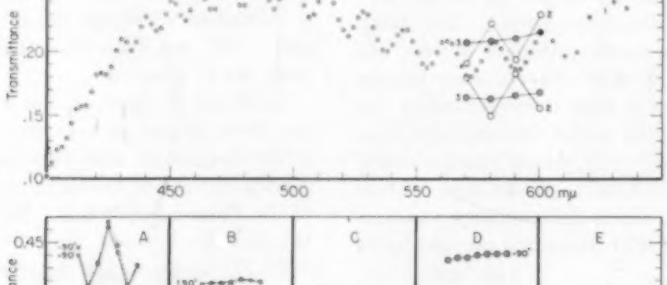


FIGURE 4.—*Effect on the measured "transmittance" of polarizing materials caused by a quartz plate cut with optic axis parallel to surfaces when placed before entrance or exit slit at various orientations (for explanation, see text).*

angles to the optic axis and apparently inserted at random, it seems well to state the following conclusions:

1. No trouble has been experienced and no errors detected relating to this effect, except in the measurement of polarizing materials.

2. To avoid important errors in the measurement of polarizing materials, the entrance quartz plate has been removed and the exit quartz lens is used only when it is necessary or desirable to collimate the beam (as when measuring thick samples or in reflection work).

3. One can readily study the effect on his instrument by carrying out measurements similar to those shown in the lower half of figure 4. By measuring the transmittance of a polarizing sample at various orientations over a short range of wavelengths, the effect can be quickly found if present.

3. Spectral-Purity Data

The spectral purity—that is, the extent of spectrum transmitted by the slits as normally used—was obtained as follows: For any given set of conditions (source, filter, phototube), with the "sensitivity" dial set three turns counterclockwise from extreme (as recommended in the instructions), and with the selector switch set at "check" (equivalent to 100.0 on the "1" scale), the slit widths in millimeters necessary to obtain a balance of the galvanometer were determined. The mechanical slit widths so determined were then multiplied by the values of millimicrons per millimeter supplied by the manufacturer.

The results are shown in figure 5. These values were obtained on the 1943 instrument. Values obtained on the second instrument are somewhat greater but otherwise similar. In either case the values are comparable with those illustrated by Cary and Beckman in their figure 9.

These slit widths are in general smaller, in some cases much smaller, than are usually practicable with commercial instruments and comprise one of the major advantages of the Beckman spectrophotometer for certain types of work. It is pointed out by the makers of the instrument that still smaller slit widths may be used if the 100-percent reading is made with the selector switch set at "1" instead of at "check". The sensitivity is, of course, decreased under this condition.

The narrowness of the slits makes unimportant for much work the fact that the operator of the instrument is limited in his freedom to set the slits at any desired width, and in normal operation they will vary as shown in figure 5. For most materials, for example, essentially the same result will be obtained whether the slits have widths equivalent to 1 or 2 mμ. However, with many of the rare-earth glasses or solutions, this is not true. Although, in general, the narrower the slits the more nearly will the measured transmission value approach the true transmission value, even on the Beckman instrument the slits are not narrow enough to make such further change negligible

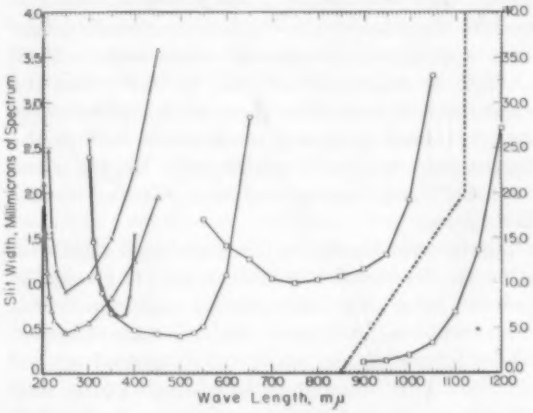


FIGURE 5.—*Approximate amounts of spectrum transmitted by the slits of a Beckman spectrophotometer under normal conditions of operation.*

△, Hydrogen, new; ▲, hydrogen, 6 hr operation; ○, incandescent, "blue" cell, with filter; ◯, incandescent, "blue" cell; □, incandescent, "red" cell.

with these materials. This is of considerable importance in chemical analytical work. In such work, in comparing results on different instruments or in analytical work with any instrument, it may be more important that the results be obtained at known slit widths than that these widths be as narrow as possible.

IV. Wavelength Calibration

The wavelength scale of the Beckman spectrophotometer provides direct reading in millimicrons. Because of the variable dispersion incident to all prism spectrophotometers, this results in greatly varying lengths of the intervals on the scale representing any given number of millimicrons as the spectrum is traversed from the ultraviolet through the visible and into the infrared. On the Beck-

man spectrophotometer the smallest scale division is equal to 0.5 mμ from 200 to 300 mμ, 1 mμ from 300 to 400 mμ, 2 mμ from 400 to 600 mμ, and 5 mμ from 600 to 2,000 mμ. (However, as pointed out elsewhere, the sensitivity of the phototube does not permit reliable measurement above 1,200 mμ, approximately.)

On a direct-reading spectrophotometer two types of wavelength checks should be considered if the greatest accuracy with the instrument is to be obtained. On the Beckman instrument one of these checks relates to adjustment of the internal screw (reached from the left end of the instrument) that rotates the collimating mirror and enables the whole wavelength scale to be brought into approximately correct adjustment. Such a check, or adjustment, should be made when the instrument is received and as often thereafter as may be found necessary or desirable. With the instruments considered in this paper the Hg green line (546.1 mμ) has proved very satisfactory for this check.

The second check on the wavelength scale relates to the small residual errors that may be present when the best average adjustment has been made by means of the adjustment screw. These errors cannot easily be eliminated and, if they are large enough to be of importance, they should be allowed for in setting the wavelength scale.

Four light sources have been used in the wavelength calibration of the instruments: (1) the quartz-mercury lamp supplied with the Beckman spectrophotometer if desired, (2) the hydrogen arc, also supplied with the instrument if desired, (3) a helium lamp (vacuum tube), and (4) a similar neon lamp.

A calibration technic was employed that gave scale corrections always on the basis of correct adjustment (zero error) at 546.1 mμ. In effect, settings with this Hg reference line were made before and after the settings with each of the numerous other lines of the various sources, 10 settings being made on each. Any deviations of the settings on the reference line from the correct value of 546.1 were allowed for in determining the deviations for the other line. In making this allowance the relative variable dispersion of the prism (as represented by the millimicrons-per-millimeter slit-width curve supplied by the makers) was taken into account.

The scale corrections thus obtained are shown in figure 6 for the two instruments. It will be noted that the Hg green line at 546.1 (the "Ref." point) has zero correction in both plots.

In studying these correction curves the millimicron equivalent of 0.1 scale division should be noted; this is shown between the two correction curves. This equivalent is also important as affecting the precision of the settings; note particularly the difference in precision above and below 600 mμ.

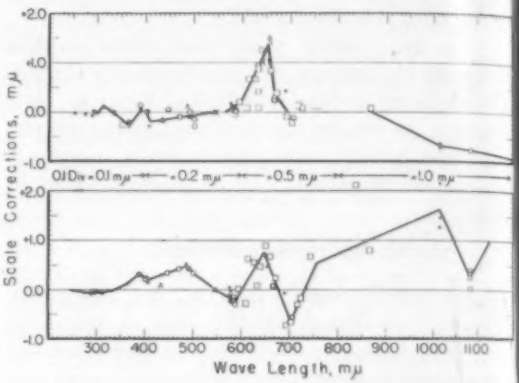


FIGURE 6.—*Residual wavelength corrections found on two Beckman spectrophotometers after adjustment of each instrument to have zero correction at 546.1 millimicrons.*

○, Hg; ◯, He; □, Ne; △, H; X, Ref.

These data are published with the thought that they may serve to inform others of the magnitudes of the wavelength errors to be expected on the Beckman spectrophotometers. They are so small that they may probably be neglected in most work for which the instruments are used. They are likewise so small that they can be determined only by the most careful work and after installing the auxiliary indicator line over the wavelength scale (see p. 604) to eliminate parallax. On the other hand these errors are large enough to be important in much of the Bureau's work, particularly when standardization is being done.

Whether or not the detailed check illustrated in figure 6 is made, it may be emphasized that check should often be made on some reference line to insure that gross wavelength errors have not developed.

V. Check of the Photometric Scale

A check of the photometric scale of a spectrophotometer independent of all other sources of error is difficult or impossible to make on most spectrophotometers. Useful for this purpose would be a series of samples whose respective transmittances do not vary with wavelength, which will not displace the beam, and for which the transmittances can be independently determined with high accuracy. No such glasses or other materials are available, however.

On a visual spectrophotometer such a check is possible by means of rapidly rotating sectors. If such sectors are properly made, the fraction of the total opening relative to 360°, that is, the effective transmittance of the sector, can be measured on a circular dividing engine with uncertainties only in the fifth decimal place. Of course, the use of such rotating sectors is based on the validity of Talbot's law. Throughout the spectrum, no certain deviations from this relation are known, however. As a matter of fact, average values obtained over a period of years in measuring the "transmittances" of accurately calibrated rotating sectors on the NBS König-Martens spectrophotometer prove both the validity of Talbot's law at various wavelengths and the reliability of the instrument over most of the photometric scale, or else there is a remarkable balancing of errors.

On photoelectric spectrophotometers, however, at least the ones considered in this paper, the use of rotating sectors to check the reliability of the photometric scale is either impossible or attended with too much uncertainty for one reason or another.

Accordingly, shortly after the advent of commercial photoelectric spectrophotometers, the National Bureau of Standards instituted the service of issuing glass standards of spectral transmittance.[11] To date, about 80 of these filters have been issued with accompanying certificates.

Three of the four types of filters used for this purpose are of moderate selectivity, covering a large part of the transmittance range from 0.00 to 0.90 at various wavelengths. A single filter thus covers a considerable part of the transmittance scale. In one sense these are inferior to strictly neutral filters in that a deviation from the true value may be due to other causes than inaccuracy of the photometric scale. On the other hand, they are superior to the neutral filters in detecting stray-light, slit-width, and gross wavelength errors.

One of the four types of filters used for these spectrophotometric standards is a fairly dense cobalt blue glass, designated as Corning G55A. (This glass is also known as Corning Signal Purple, present catalog designation 5551.) The 30-mm disks cut from the original roundel were recently exhausted, and it became necessary to prepare new samples from a new roundel. This of course required an extensive series of measurements in order that values of transmittance might be determined with satisfactory certainty. (After basic values are thus determined for selected disks from a given roundel, values of spectral transmittance for other disks cut from this roundel can be determined with much less labor, as noted below).

About the time that these measurements were necessitated, the second Beckman spectrophotometer was received. It was decided that an excellent opportunity was thus presented for (1) making a fairly thorough check of the reliability of transmittance measurements made on the Beckman spectrophotometer as it was received from the manufacturer, and (2) if no consistent errors appeared to be present in the Beckman data thus obtained, increasing the over-all reliability of the basic spectral-transmittance values for the new glass disks. Only three things were done to the second Beckman instrument for these measurement—the quartz lens over the exit slit was removed to eliminate multiple-reflection errors, a careful check of the wavelength calibration was made after installation of the second indicator line, and the temperature-control sample holder constructed at the Bureau was used, all as previously noted.

Corresponding work with the first Beckman spectrophotometer received in 1943 had not been done for two reasons: (1) the urgency of other work made it impossible to devote the necessary time for such measurements as long as the original supply of spectrophotometric standards held out, and (2) trouble was experienced in readings obtained with the cesium-oxide phototube, particularly at low transmissions, in that there was excessive and erratic "creep" of the galvanometer needle, and a definite and trustworthy reading at these low transmittances could seldom be obtained. Changing phototubes did not remedy the trouble.

[11] K. S. Gibson, Geraldine K. Walker, and Mabel E. Brown, Filters for testing the reliability of spectrophotometers, J. Opt. Soc. Am. **24**, 58 (1934).

Similar trouble was not experienced with the cesium-antimony phototube or with either phototube circuit on the new instrument.

Among the many disks cut from the second G55*A* roundel, designated as G55A*β*, were two which were identical in spectral transmittance, and a third which was also identical over part of the range. The identity of these spectral transmittances was established within about 0.1 percent of the transmittance by comparative measurements on the Beckman spectrophotometer.

Measurements were accordingly made on each of these glasses by each of the authors, on the Beckman, the König-Martens visual [12] and the Gibson photoelectric [13] spectrophotometers, and at the various wavelengths in the visible spectrum indicated in table 1. The temperature of the sample was kept at 25° C for all the measurements, so that this source of variation or uncertainty was eliminated.[14]

[12] H. J. McNicholas, Equipment for routine spectral transmission and reflection measurements, BS J. Research **1**, 793 (1928) RP30.

[13] K. S. Gibson, Direct-reading photoelectric measurement of spectral transmission, J. Opt. Soc. Am. & Rev. Sci. Instr. **7**, 693 (1923).

[14] The General Electric recording spectrophotometers were not used in this standardization of the G55A*β* glass because (1) no temperature control has been devised for use on these spectrophotometers, and (2) the slit widths are undesirably large for this type of work.

TABLE 1.—*Values of transmittance as measured with the Beckman, König-Martens, and Gibson spectrophotometers*

Sample: Corning G55A*β* of 3-mm thickness; temperature: 25° C.

Wavelength	Source	Stray-light filter	Beckman			König-Martens			Gibson			Adopted values of transmittance	Computed huge error (=4.9× probable error)
			Number of determinations	Average transmittance	Average deviation	Number of determinations	Average transmittance	Average deviation	Number of determinations	Average transmittance	Average deviation		
mμ													
390	Incandescent	Yes	4	0.8949	.0012	-----	-------	-------	4	0.08976	0.0019	0.895	0.0032
	do	No	4	.8909	.0011	-----	-------	-------	-----	-------	-------		
404.7	Mercury	No	4	.8824	.0016	-----	-------	-------	-----	-------	-------	.884	.0040
	Incandescent	No	4	.8909	.0016	-----	-------	-------	-----	-------	-------		
	do	Yes	-----	-------	-------	-----	-------	-------	4	.8890	.0010		
435.8	Mercury	No	4	.8059[a]	.0009	-----	-------	-------	-----	-------	-------	.806	.0016
	Incandescent	No	4	.8045	.0015	-----	-------	-------	4	.8075	.0005		
	Mercury	Yes	-----	-------	-------	5	0.8043	0.0011	-----	-------	-------		
471.3	Incandescent	No	4	.6114	.0021	-----	-------	-------	4	.6182	.0008	.612	.0058
		Yes	-----	-------	-------	4	.6064	.0009	-----	-------	-------		
491.6	do	No	4	.3406	.0021	-----	-------	-------	4	.3466	.0012	.344	.0033
		Yes	-----	-------	-------	4	.3438	.0018	-----	-------	-------		
501.6	do	No	4	.2430	.0028	-----	-------	-------	4	.2480	.0010	.245	.0030
	Helium	No	-----	-------	-------	4	.2435	.0007	-----	-------	-------		
520	Incandescent	No	6	.0905	.0008	-----	-------	-------	6	.0901	.0014	.091	.0010
		Yes	-----	-------	-------	6	.0916	.0007	-----	-------	-------		
540	do	No	6	.0305	.0006	6	[a].0310	.00017	6	.0308	.0006	.0308	.00045
546.1	Mercury	No	4	.0335	.0001	4	[a].03355	.00006	-----	-------	-------	.0335	.00021
	Incandescent	No	4	.0332	.0004	-----	-------	-------	4	.0337	.0004		
560	do	No	6	.0646	.0004	6	[a].0630	.00018	6	.0642	.0005	.064	.00074
578	Mercury	No	4	.0271	.0003	4	[a].02723	.00015	(4)	(.0284)	(.0004)	.0273	.00044
	Incandescent	No	4	.0281	.0002	-----	-------	-------	-----	-------	-------		
600	do	No	[b](6)	(.0075)	(.0001)	7	[a].00743	.00012	-----	-------	-------	.0074	.00020
		Yes	(2)	(.0072)	(.0002)	-----	-------	-------	-----	-------	-------		
		No	(6b)	(.0106)	(.0002)	7	[a].01003	.00011	-----	-------	-------		
620	do	No	(6r)	(.0130)	(.0007)	-----	-------	-------	-----	-------	-------	.0100	.00021
		Yes	(2b)	(.0096)	(.0004)	-----	-------	-------	-----	-------	-------		
		Yes	(2r)	(.0100)	(.0002)	-----	-------	-------	-----	-------	-------		
		No	(2b)	(.0084)	(.0001)	-----	-------	-------	-----	-------	-------		
640	do	No	(4r)	(.0100)	(.0006)	-----	-------	-------	-----	-------	-------	.0074	.00022
		Yes	(2b)	(.0070)	(.0003)	5	[a].00743	.00010	-----	-------	-------		
		Yes	(2r)	(.0081)	(.0007)	-----	-------	-------	-----	-------	-------		
667.8	do	No	4	.0338	.0006	-----	-------	-------	(4)	(.0371)	(.0011)	.034	.0011
		Yes	-----	-------	-------	4	[a].0337	.0008	-----	-------	-------		
680	do	No	4	.136	.003	-----	-------	-------	4	.137	.006	.14	.008
690	do	No	4	.342	.007	-----	-------	-------	4	.345	.012	.34	.015
		Yes	-----	-------	-------	(4)	(.321)	(.009)	-----	-------	-------		
706.5	do	No	4	.7136	.0047	-----	-------	-------	4	.7110	.0015	.713	.0056
720	do	No	4	.8449	.0014	-----	-------	-------	4	.8455	.0018	.845	.0024
750	do	No	4	.9015	.0010	-----	-------	-------	4	.9016	.0014	.901	.0018

[a] Rotating sector used in blank beam.

[b] Values in parentheses were not used in deriving the adopted values of transmittance nor in computing the huge errors.

In table 1 are given for each of the three instruments, at each of the respective wavelengths, the number of determinations of transmittance made, the average value of the transmittance so measured, and the average deviation of each determination from the average value. On the Beckman and Gibson spectrophotometers, each determination consists of two or more readings with separate wavelength settings. On the König-Martens spectrophotometer a determination is derived from 20 photometric settings, 10 with the sample in each beam. In columns 2 and 3 and in the footnotes are indicated certain experimental conditions pertinent to the determinations. In the last two columns are given the basic values of transmittance adopted from the measurements for the NBS standard glass, together with the "huge error" (4.9 times the probable error) [15] as computed from the deviations of the several separate determinations from this adopted value. Eight or more determinations always entered into the computation of this huge error.

In a consideration of the data of table 1, the following points should be noted:

1. The König-Martens and Gibson spectrophotometers were used in the usual routine manner.

2. As part of the purpose of these measurements was a test of the Beckman instrument, measurements were made at all wavelengths. On the other two instruments measurements were not made at those wavelengths which long experience has indicated to be relatively unreliable. This obviously applies to the violet and red ends of the spectrum with the König-Martens visual spectrophotometer. For this type of glass with the Gibson spectrophotometer it applies to the region from 600 to 660 mμ, where the transmittance is extremely low and stray energy renders the values relatively unreliable; this stray-energy error is believed to affect the values for this glass measured on this instrument at 578 and 667.8 mμ also.

3. The same sort of error is apparent in the data obtained with the Beckman spectrophotometer in the region of very low transmittance with this glass, though apparently to a less extent. In both instruments this is the region in which the "blue sensitive" and the "red sensitive" phototubes give about the same response—near 590 mμ on the Gibson and near 625 mμ on the Beckman. Normally, in either case the phototube giving the greatest response is used in the measurements. For most types of samples either instrument, with the appropriate phototube, will give as accurate results through this region as at other regions. With this glass, however, for which the transmittance being measured is very low and for which the transmittance is high at those spectral regions in which the phototube is much more sensitive, the freely transmitted stray energy from these regions may produce an important error. On the Beckman spectrophotometer this was checked by the use of stray-energy filters—Corning 2424 with the "blue sensitive" phototube from 600 to 640 mμ and a Corning medium Aklo with the "red sensitive" phototube from 620 to 640 mμ. It can be seen that the measured transmittance is lowered and on the average comes close to the values obtained with the König-Martens spectrophotometer.

4. The three instruments for which data are given in table 1 differ in the number of decimal places which can be obtained in the transmittance, T.

(a) Values of T on the Gibson spectrophotometer can be read to only 0.001, or at most 0.000_5. However, this reading is definite as a vernier is provided on the reading scale of the rotating sector. For low transmittances the number of significant figures is therefore limited, and the fourth decimals given in the table result simply from the averaging.

(b) On the Beckman instrument, values of T can be read to 0.001 by estimating tenths of a division, or on the same dial to 0.0001 for values of transmittance less than 0.11 if the selector dial is set to ".1". This greatly facilitates making the reading, but otherwise there appears to be little gain in the use of the magnified scale. Slight and erratic "creeping" of the galvanometer often makes it uncertain when the best reading is obtained. The authors have been able to obtain the precision indicated by the average deviations shown in table 1 for these low values only by consistent checking of the "off" reading, bringing the transmittance reading to such a value that the galvanometer position is identical for the two juxtaposed readings.

[15] Mansfield Merriman, A textbook on the method of least squares, 8th ed., rev., p. 205 (John Wiley & Sons, Inc., New York, N. Y., 1915). Peter's approximation formula was used to compute probable errors.

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(c) On the König-Martens spectrophotometer, the photometric settings are read to tenths of a degree (by vernier if desired) and transmittances computed by the cot $\times$ tan relation. The normal number of significant figures is three for transmittances greater than 0.10, although four are often kept temporarily. When the "10%" sector (T= 0.09945) is used in the blank beam, the same number of significant figures is obtained but the uncertainty as represented by the average deviation has been moved to the fourth decimal place. With the "1%" sector (T=0.00883) there is another displacement of the significant figures, but the lowered brightness may result in slight uncertainty still in the fourth decimal.

5. The precision or reproducibility of readings of the Beckman spectrophotometer, as judged by the average deviations, is comparable to that of the other instruments, except that the König-Martens is better than either the Beckman or the Gibson instruments at the low values of T, as already discussed. It should be noted that each of the four to six determinations at each wavelength on the various spectrophotometers was made on a different day, this work extending off and on over a period of weeks. The reproducibility of either photoelectric instrument at any one time and wavelength setting is in general superior to that indicated in table 1. The Beckman is the most rapid of the three instruments, being somewhat superior in this respect to the Gibson and greatly superior of course to the König-Martens (visual).

6. No error in the photometric scale of the Beckman spectrophotometer can be demonstrated by the data of table 1. The following details may be noted:

(1) The consistent differences between results by the Beckman and the Gibson spectrophotometers at the shortest wavelengths are not representative of results always obtained on these instruments at these wavelengths. For example, see below in connection with the results of table 2.

(2) Except at 390 and 404.7 mμ, the average value at each wavelength obtained on the Beckman either lies between the values obtained on the other instruments or agrees closely with one of them. This holds even at the low values at 620 and 640 mμ when the stray-energy filters are used.

(3) The use of the Hg source at the four wavelengths noted has proved very satisfactory. After a short warming-up period the lamp becomes steady. The slit widths are larger than with the incandescent source, but this is of no consequence as the light is homogeneous. It may be noted that in every case the values obtained with the Hg source are closer to the finally adopted values than those obtained at the same wavelength with the incandescent source. The values obtained with the Hg source are not subject to wavelength error or to as great a stray-energy error

TABLE 2.—*Comparison of average transmittance obtained with the Beckman spectrophotometer with those adopted from extensive measurements on the Beckman, König-Martens, and Gibson spectrophotometers*

[Samples: Jena BG 14 (Green) and Corning HT (Yellow C), each of 2-mm thickness. Temperature: 25° C. Measurements by Lois A. Peterson]

Wave length	Adopted transmittance		Deviation of average Beckman value from adopted transmittance	
	Jena BG14	Corning HT Yellow C	Jena BG14	Corning HT Yellow C
mμ				
390	0.862	0.025	0.000	0.001
404.7	.877	.020	.000	−.001
420	.....	.019	.....	.000
435.8	.893	.0240	.000	.0003
471.3	.894	.081	.001	.000
501.6	.859	.208	.001	−.001
520	.....	.316	.....	.001
530	.760	.379	−.001	−.001
546.1	.671	.479	.001	−.001
560	.585	.557	−.002	.002
578	.473	.636	−.001	.000
587.6	.....	.668	.....	.000
600	.350	.690	−.001	.000
620	.256	.731	.001	.000
640	.187	.747	.001	.002
660	.....	.754	.....	.000
667.8	.122	.....	.000	.....
690	.....	.755	.....	−.001
710	.074	.....	.001	.....
720	.....	.748	.....	−.001
750	.057	.730	.000	−.001
800	.051	.693	.000	.000
850	.057	.....	.000	.....
900	.072	.631	.001	+.001
950	.094	.....	.000	.....
1000	.124	.600	.001	.000

(4) At all but the lowest transmittances, the values obtained on the Beckman instrument differ from the finally adopted values by amounts that (1) are less than the uncertainties of the adopted values, and (2) do not exceed 1 percent of the value.

7. The adopted values and huge errors shown in the table are similar to those certified on the G55A standards of spectral transmittance issued by the National Bureau of Standards, except

that in the certificates the huge errors are designated by the term "uncertainty" and are reported to the same number of decimal places as the transmittance itself.

In further confirmation of the reliability of the photometric scale of the Beckman spectrophotometer are results obtained more recently by Lois A. Peterson of the Photometry and Colorimetry Section, with two others of the NBS standards of spectral transmittance, a Jena green glass and a Corning yellow glass. The same spectrophotometers were used as for the work on the blue glass standard just described, and the number of determinations, the uncertainties, and the various other factors entering into the measurements were all comparable with those listed above. No stray-energy filter was used on the Beckman except at 390 mμ.

The results are shown in table 2, in which are given for each standard (1) the adopted (usually the average) values obtained as a result of the extensive measurements on the three spectrophotometers (except that the visual determinations do not extend beyond 435.8 and 667.8 μ), and (2) the deviations of the average Beckman values from these adopted values. Examination of these data shows that there is no consistent deviation of the spectral transmittances obtained on the Beckman spectrophotometer from those obtained on the other instruments.

In addition to the general over-all reliability of the Beckman spectrophotometer demonstrated above, special note may be made of the precision and reliability with which two nearly identical samples may be spectrophotometrically compared. In this case the "100%" reading is taken with a standard sample in the beam (instead of with the beam blank or with a solvent cell in the beam) and the only condition that has been changed to obtain balance is that the slits have been widened. Of course, the lower the transmittance the wider must the slits be for balance, but as this width will vary inversely as the square root of the transmittance they will be only about 10 times the normal width when the transmittance is as low as 0.01.

For comparing two nearly identical samples such widths are not at all excessive. As a result, if accurately calibrated standards are available, such as the three glasses to which reference has been made above, the spectral transmittance of similar glasses may be determined in a very short time with an accuracy comparable to that of the standard, even for the very low transmittances. In other words, the comparison can be made with uncertainties of but 0.1 or 0.2 percent of the transmittance, regardless of whether this is near 0.9 or 0.01.

An additional important feature of these narrow slits is that low transmittances can be determined by a "step-down" procedure, in which, for example, a glass transmitting 10 percent may be measured and used as standard for a glass transmitting 1 percent, that in turn for a glass transmitting 0.1 percent, and so on. On the Beckman instrument the slits do not become excessively large in this procedure.

VI. Conclusions

On the basis of measurements made mostly on a Beckman spectrophotometer received in the Photometry and Colorimetry Section of the National Bureau of Standards in 1945, it appears that the instrument is capable of precise and accurate measurement of spectral transmittance or transmittancy. This conclusion is based on measurements of the spectral transmittance of certain glass standards on the Beckman, the König-Martens, and the Gibson spectrophotometers. The measurements were limited to the spectral range from 390 to 750 mμ, but there seems no reason to doubt the reliability of transmission data obtained on the Beckman instrument at wavelengths beyond this range—to approximately 1,000 mμ in the infrared, and to either 320 or 210 mμ in the ultraviolet, depending on the source and phototube used in the instrument.

On all three instruments the glass samples were kept at 25° C, being mounted in temperature-control boxes constructed at the National Bureau of Standards. The general statement of reliability given above is also dependent on careful check of the wavelength scale and on adjustment or correction of any errors greater than about 0.1 mμ. Furthermore, it applies only to values of transmittance from 1.00 to about 0.02. Below 0.02 there is no demonstrated error in the photometric scale, but definite reproducible results for values in this region have not always been obtainable.

If the $-\log_{10}T$ scale is used, large uncertainties may thus be present if values of the order of $-\log_{10}T=2.0$ are being measured. Where possi-

ble it would be preferable to adjust solutions so that absorbancies greater than 1.0 or 1.5 need not be measured.

The slit widths normally used on the Beckman spectrophotometer are believed to be less than those on any other commercial spectrophotometer. For spectral-transmission measurements these widths normally are such as to transmit from 0.5 to 1.5 mμ of spectrum within the range 220 to 950 mμ when the appropriate source and phototube are used. This feature of the instrument serves three useful purposes. It enables the spectral transmission of samples having high selectivity to be determined with an accuracy unattainable with instruments having wider slits. It makes possible the precise and accurate comparison of nearly identical samples, even those having high absorption, without the use of slits unduly wide. It makes possible the reliable determination of very low transmittances by a step-down procedure with samples of intermediate transmittance.

As with any spectrophotometer the wavelength calibration should be carefully checked when the instrument is received and as often thereafter as may be found necessary. The mercury green line at 546.1 mμ has proved to be a good reference line for adjustment purposes. When this wavelength is correctly adjusted, errors in the rest of the scale exceeding 0.5 mμ were not found on either of the instruments considered, except above 600 mμ, where the dispersion is relatively small.

As with any single-dispersion spectrophotometer stray-energy errors will usually be present in the regions of low spectral response. The filter supplied by the makers of the Beckman instrument should always be used in the region from 320 to 400 mμ with incandescent source. Other filters may be desirable for certain types of transmission or for other special reasons. Multiple reflection effects should be considered if errors less than 1 percent are considered important.

The instrument is subject to error if a fluorescent sample is measured. The magnitude of this error will depend on the ratio of fluorescent to incident energy and on the inter-relation of the photocell sensitivity and the wavelength regions of excitation and fluorescence. If the fluorescent energy is in the visible region, it can be detected by placing the sample in the beam and viewing it from above as the wavelength is varied through the ultraviolet and visible regions. One can thus be forewarned. If the fluorescence is in the ultraviolet, such error would be difficult to detect without special equipment for the purpose. The error can be much greater in reflection than in transmission measurements.

Care should be taken in the measurement of the transmittance of polarizing materials. Two effects may be noted. As with all prism instruments the energy transmitted by the dispersing prism becomes partially polarized. As a result, the value of transmittance obtained will depend on the orientation of the polarizing sample being measured. A second and more serious effect may arise if the quartz plate over the entrance slit (and to a much less extent the quartz plate or lens over the exit slit) is cut with the optic axis parallel to the surfaces of the plate. Serious distortions of the transmittance curve may result, as shown in figure 4.

In conclusion, therefore, it may be stated that spectral-transmission measurements of high reliability are obtainable on the Beckman quartz spectrophotometer. To obtain such results, however, one must take various precautions. The instrument is convenient and rapid to use and covers a wavelength range not heretofore readily available in a single instrument.

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Mass-Spectrometer Study of the Rare Gases

By Vernon H. Dibeler; Fred L. Mohler, and Robert M. Reese

A study of the appearance potentials and isotope abundance of the rare gases has been made with a Consolidated Engineering Corp. mass spectrometer as a check on the operation of the instrument. The results are comparable to previously published data. In addition, some new experimental values of ionization potentials have been obtained. Generally, good agreement of the isotope abundance measurements with previously published values obtained on other types of instruments and with chemically determined atomic weights, indicates a minimum of discrimination effects. The relative values of the ion currents for the rare gases were obtained and plotted against the atomic number. No simple relation between sensitivity and atomic number is evident.

I. Introduction

Mass spectrometer studies of all the rare gases have been published. Bleakney [1],[1] and more recently Stevenson and Hipple [2], have measured the appearance potentials of singly and multiply charged ions in helium, neon, and argon. Nier [3], Aldrich and Nier [4], and Vaughan, Williams, and Tate [5] have published accurate values of the isotope ratios of the rare gases. A survey of all the rare gases with a Consolidated Engineering Corporation mass spectrometer was primarily undertaken by the authors as a check on the performance of the instrument. As the results supplement published work in several respects, and as a precision has been obtained that is comparable with the best published work, it seemed worth while to publish the results. The relative values of ion currents obtained under similar conditions in a series of gases having similar electronic structure but differing in atomic weight are of interest. Some new values of ionization potentials have also been obtained. The observed values of the isotope ratios serve further to corroborate accepted values of isotope ratios and computed atomic weights. Some recent papers by Coggeshall [6] and Washburn and Berry [7] concerning discrimination in the ion source indicate that this may appreciably influence observed isotope ratios. In this connection, a comparison of the results obtained by different types of instruments is useful.

[1] Figures in brackets indicate the literature references at the end of this paper.

II. Experimental Procedure

The Consolidated mass spectrometer used in the present work has been described elsewhere [8]. Briefly, it consists of a tungsten-filament source of electrons, the energies of which can be controlled between 0 and 100 v by a wire-wound potentiometer and measured to ± 0.5 percent by a calibrated voltmeter. The positive ions formed in the electron beam are drawn out by a fixed potential of about 3 v for appearance potential measurements, whereas a variable potential (approximately 1 percent of the ion accelerating voltage) is used in the isotope abundance measurements. The positive ions are then accelerated by a variable electric field and deflected into 180-degree arcs by a suitable magnetic field. They are separately amplified by an electrometer tube and recorded by galvanometers. The recorder contains four galvanometers in parallel with sensitivities in the ratios of 1 : 3 : 10 : 30. Thus the 8-in. photographic record has an effective width of 240 in.

The appearance potential measurements were made in the usual manner and evaluated according to the method of "initial breaks" described by Stevenson and Hipple [9].

Whenever possible, the isotope abundance measurements were made at several different pres-

sures and values of electron energy and current. Lack of discrimination in the apparatus was shown by indepedence of the abundance ratios of these values [3].

The rare gases used in this investigation were portions of samples submitted to this laboratory for mass spectrometric analysis by the Bureau of Mines helium plants and the Air Reduction Sales Co. All were of greater purity than 99.5 percent by volume, the helium containing less than 0.1 percent by volume of total impurity.

III. Discussion of Results

1. Ionization Potentials

Figure 1 shows the initial portions of the ionization efficiency curves for the singly charged ions of helium and neon and the singly and doubly charged ions of argon. Their critical potentials are summarized in table 1 and compared with some previously reported data obtained both by electron impact and by optical methods. The doubly charged helium ion was not measured because of interference by H_2^+ ion. The hydrogen was possibly released from the interior surfaces of the mass spectrometer when helium was admitted as background runs showed no trace of H^+ ion or H_2^+ ion. To simplify the figure, the doubly charged neon curve is not shown. It has a very low intensity with an attendant increase in error of the determination of the appearance potential. The slope of the ionization efficiency curve for doubly charged argon continues to increase for approximately 9 v after the initial break, whereas that portion of the curve for singly charged argon is about 2.5 v. This agrees with observations reported by Stevenson and Hipple [2]. The observed critical potentials are in good agreement with computed values in spite of the shape of the curves.

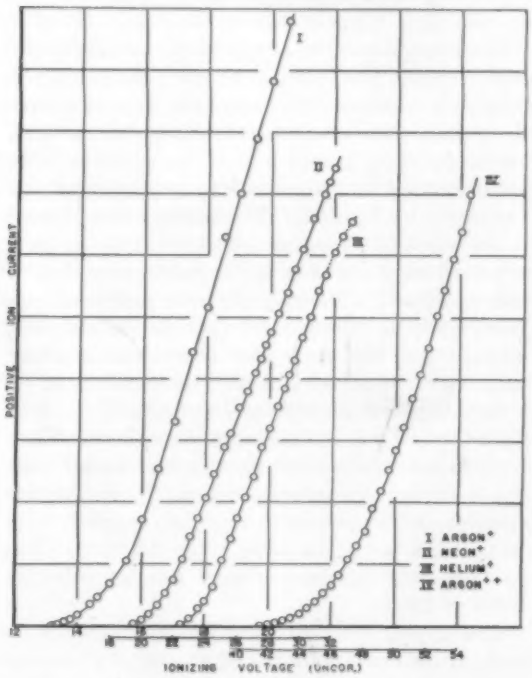

FIGURE 1.—*Initial portions of the ionization efficiency curves for the ions* He^+, Ne^+, A^+, *and* A^{++}.

The ordinate is arbitrary and different for some ions. The middle scale of the abcissa applies to curves II and III. The lower scale applies to curve IV.

TABLE 1.—*Appearance potentials of singly and multiply charged ions of the rare gases relative to* A^+

[Appearance potential, volts]

Ion	This paper[a]	Optical sources[b]	Others
He^+	$24.4_6 \pm 0.2$	24.586	
Ne^+	$21.5_5 \pm 0.1$	21.58	21.5±0.1 [1].
Ne^{++}	61.7 ±2.0	62.7	63.0±0.5 [1].
			$(Ne^+)-(A^+)=5.6_3\pm0.15$ [3].
A^+	[c] 15.76	15.76	15.7±0.1 [1].
			$(A^{++})-(A^+)=28.0\pm0.5$ [3].
A^{++}	$43.6_1 \pm 0.2$	43.62	44.0±0.5 [1].
Kr^+	$13.9_8 \pm 0.1$	14.009	
Kr^{++}	38.6 ±0.2	38.6 [12]	
Xe^+	$12.1_6 \pm 0.1$	12.138	
Xe^{++}	34.1 ±0.2	33.3 [13]	

[a] Corrected scale, assuming $I(A^+)=15.76$ ev.

[b] Bacher and Goudsmit, Atomic energy states (McGraw-Hill Book Co., New York, N. Y., 1932). Conversion factor 8,066 cm^{-1} used to convert from wave numbers to electron volts.

[c] Observed value is $13.4_6 \pm 0.1$ v.

Figure 2 shows the initial portions of the ionization efficiency curves for singly and doubly charged ions of krypton and xenon. The plots for Kr^{++} ion and Xe^{++} ion are, like A^{++} ion, curved over a range of 8 to 10 v beyond the appearance potential.

2. Isotope Abundance Ratios

The measurement of the ratio of He^3 to He^4 is beyond the range of the Consolidated mass spectrometer, but has been measured by Aldrich and Nier [4] as 1.7×10^{-6}. They used a mass spectrometer

of sufficient resolving power to show that the mass 3 peak was not HD.

Table 2 lists the neon isotopes and the percentage abundance as determined in this laboratory and by Vaughan, Williams, and Tate [5]. The maximum deviation in the tables in this paper is intended only as an indication of the reproducibility of the measurements. The accuracy is believed to be of the order of 1 percent of the abundance for isotopic abundances greater than 10 percent. With the neon isotopic masses listed by Pollard [10] and converting from the atomic to the chemical scale, a chemical weight of 20.18_2 is obtained. The accepted value is 20.183 (International Atomic Weights, 1947).

TABLE 2.—*Abundance of isotopes of neon*

	m/e		
	20	21	22
	Percent	*Percent*	*Percent*
This paper	90.51	0.28	9.21
Maximum deviation	±0.15	±.02	±0.18
Vaughan, Williams, and Tate [8]	90.0	.27	9.73

Table 3 lists the argon isotopes and their respective percentage abundance. The comparative data are again those of Vaughan, Williams, and Tate [5], and the weight calculated from their values is 39.95_0. The accepted value is 39.944. The chemical weight computed from the abundance and the isotopic weights given by Pollard [10] is 39.94_9.

TABLE 3.—*Abundance of isotopes of argon*

	m/e		
	36	38	40
	Percent	*Percent*	*Percent*
This paper	0.35	0.08	99.57
Maximum deviation	±.01	±.01	±0.03
Vaughan, Williams, and Tate [8]	.307	.061	99.632

Table 4 lists the krypton isotopes and their respective abundance. Nier's values [3] converted from relative to percentage abundance are also included. The calculation of the chemical weight was made by using Aston's isotopic masses of krypton [11] and gives the value 83.80. Nier's values give a weight of 83.81. The accepted value is 83.7.

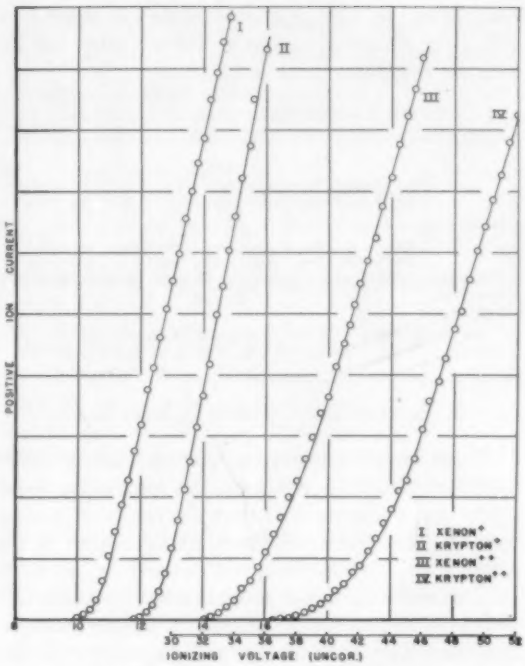

FIGURE 2.—*Initial portions of the ionization efficiency curves for the ions* Kr^+, Kr^{++}, *and* Xe^{++}.

The ordinate is arbitrary and different from some ions. The lower scale of the abcissa applies to curves III and IV.

TABLE 4.—*Abundance of isotopes of krypton*

	m/e					
	78	80	82	83	84	86
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
This paper	0.36	2.25	11.57	11.44	57.14	17.24
Maximum deviation	±.01	±0.02	±0.04	±0.03	±0.03	±0.05
Nier [3]	.35	2.01	11.53	11.53	57.11	17.47

Table 5 lists the xenon isotopes and their respective percentage abundance. Again Nier's values [3] are included for comparison. The rather serious disagreement of the abundance of mass 130 may be due to the lower degree of resolution obtainable in the mass spectrometer used in this work compared to Nier's apparatus. Assuming a packing fraction of −5.3 [11] and

converting to the chemical scale, a weight of 131.3_2 is obtained. Nier's values give 131.29, and the accepted value is 131.3.

TABLE 5.—*Abundance of isotopes of xenon*

	m/e								
	124	126	128	129	130	131	132	134	136
	Per-cent	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*
This paper	0.102	0.098	1.93	26.51	3.68	21.04	27.12	10.54	8.98
Maximum deviation	±.009	±.003	±0.01	±0.02	±0.04	±0.09	±0.07	±0.05	±0.03
Nier [3]	.094	.088	1.90	26.23	4.07	21.17	26.96	10.54	8.95

3. Relative Ion Currents in Rare Gases

These measurements on the rare gases afford an opportunity to compare the ionization sensitivity for elements with a wide range of atomic number but similar electron configuration in the outer shell. "Sensitivity" is defined as the number of scale divisions of galvanometer defection per unit pressure (in microns) in the gas-inlet system. The sum of the deflections for all isotopes has been used, as in this case we are not concerned with the partial pressures of the separate isotopes. The pressure in the ionization chamber is probably very nearly proportional to the pressures in the inlet system. The ionizing electrons had an energy of about 70 v. Figure 3 and table 6 give data on sensitivity versus atomic number. The results indicate that there is not a simple relation between atomic number and sensitivity. Instrumental discrimination may slightly distort the relative values for light atoms as compared with heavy ones, but the effect would scarcely exceed a few percent.

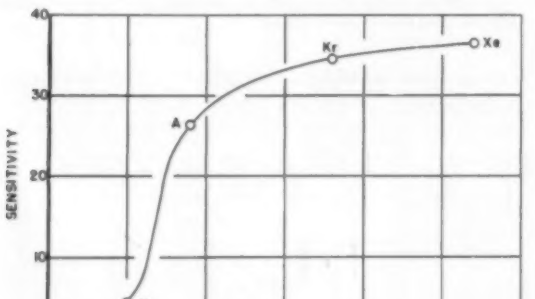

FIGURE 3.—*Number of recorder scale divisions per micron of sample pressure versus the atomic number for the singly charged ions of* He, Ne, A, Kr, *and* Xe.

Ordinates are the sum of deflections for all isotopes.

TABLE 6.—*Ion sensitivity of the rare gases as a function of the atomic number*

Ion	Atomic number	Sensitivity	
		Divisions/micron	Relative to helium
He^+	2	1.4	1.0
Ne^+	10	4.2	3.0
A^+	18	26.5	18.9
Kr^+	36	35.0	25.0
Xe^+	54	37.5	26.8

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Hydrocarbons in the 102° to 108° C Fraction of Petroleum[1,2]

By Augustus R. Glasgow, Jr., Charles B. Willingham, and Frederick D. Rossini

This report describes the analysis of the hydrocarbons in the 102° to 108° C aromatic-free fraction of petroleum, which is shown to be composed substantially of the following three compounds (normally boiling at the temperature indicated): Ethylcyclopentane at 103.5° C; 1,1,3-trimethylcyclopentane at 104.9° C; and 2,2-dimethylhexane at 106.8° C. The amounts of these three compounds in the original Ponca, Okla. crude petroleum are estimated to be, respectively, 0.1$_5$, 0.3$_5$, and 0.01 percent by volume.

I. Introduction

In continuation of the work of the American Petroleum Institute Research Project 6 at the National Bureau of Standards on the fractionation and analysis of hydrocarbons in petroleum [1],* work was completed on the resolution of that part of the petroleum normally boiling between 102° and 108° C. On the assumption that the possible components in the original crude petroleum are hydrocarbons of the paraffin, cyclopentane, cyclohexane, and aromatic series, the aromatic-free fraction of petroleum of this boiling range could contain only the following three compounds.[3] Ethylcyclopentane at 103.5° C, 1,1,3-trimethylcyclopentane at 104.9° C, and 2,2-dimethylhexane at 106.8° C. The earlier work in this laboratory [5] on the material of this boiling range was handicapped by lack of the highly efficient means of distillation available for the present investigation [6].

This report describes the analysis of the hydrocarbons in the 102° to 108° C aromatic-free fraction of petroleum, which is shown to be composed substantially of the above-mentioned three compounds.

II. Material Analyzed

The American Petroleum Institute Research Project 6 at the National Bureau of Standards has had under investigation since 1928 a large quantity of petroleum taken from a well at Ponca, Okla. [1, 7]. The material analyzed in the present investigation constituted that part of this original petroleum normally boiling between 102° and 108° C. From this petroleum there has previously been separated methylcyclohexane (at 100.9° C) [8] and toluene (normally boiling at 110.6° C but actually spread over much lower boiling material) [9]. The status of the material normally boiling in the range 102° to 108° C prior to the present investigation, is described in reference [5]. Before the beginning of the present investigation, the material was made aromatic-free by filtration through silica gel [10].

III. Method of Analysis and Separation

The material of the original petroleum remaining after the previous treatment [9, 8, 5] was "lined-up" by appropriate preliminary distilla-

[1] This investigation was performed as part of the work of the American Petroleum Institute Research Project 6 at the National Bureau of Standards on the "Analysis, Purification, and Properties of Hydrocarbons."

[2] Presented before the Division of Petroleum Chemistry of the American Chemical Society at the meeting at Atlantic City, N. J., April 1947.

[3] At the time the first highly efficient analytical distillation of the 102° to 108° C fraction of petroleum was completed in this laboratory in 1942, the existing data in the literature [2, 3] listed 1,1,3-trimethylcyclopentane as normally boiling at 115 to 116° C. It had originally been expected, therefore, that only two compounds, easily separable, would appear in the distillate. But a third compound appeared, having a normal boiling point about 1½° C above ethylcyclopentane, with a slightly lower, but still high, refractive index, indicating the new compound to be a cycloparaffin. It was deduced that the latter could only be a C_8 alkylcyclopentane, and, further, that the only possible C_8 alkylcyclopentane normally boiling near 105° C was 1,1,3-trimethylcyclopentane, the existing literature data to the contrary notwithstanding. These deductions were shortly thereafter confirmed by new data published on the synthesis and properties of 1,1,3-trimethylcyclopentane [4].

* Figures in brackets indicate the literature references at the end of this paper.

tions and blending in order to obtain in one lot of material all the remaining original petroleum normally boiling between 102° and 108° C.

Following the preliminary distillation and blending, five distillations (regular or azeotropic) were performed at high-efficiency and high reflux ratio, as listed in table 1. From appropriate final distillations of this series, small "best lots from petroleum" for ethylcyclopentane, 1,1,3-trimethylcyclopentane, and 2,2-dimethylhexane were selected for measurement of physical properties and determination of purity.

The purity of the two cycloparaffins, of which there was a sufficient quantity to produce a relatively pure best lot from petroleum, was evaluated from measurement of the freezing points. For 2,2-dimethylhexane the quantity was so small as to make impracticable the isolation of a samp high purity, and the amount of 2,2-dimethylhe in its best lot from petroleum was estimated f its values of refractive index and density as c pared with those of pure 2,2-dimethylhexane the probable contaminants, as made evident f the results of the analytical distillation (see fig.

The best lots from petroleum of ethylcyclo tane and 1,1,3-trimethylcyclopentane and second-best lot of 2,2-dimethylhexane were examined spectrographically with an infr spectrometer [1] by the Socony-Vacuum Labo tories, using the appropriate NBS Stand Samples of hydrocarbons for calibration.

The relative amounts of the three compou in the Ponca, Okla., petroleum are taken from

[1] A description of this instrument is given in reference [11].

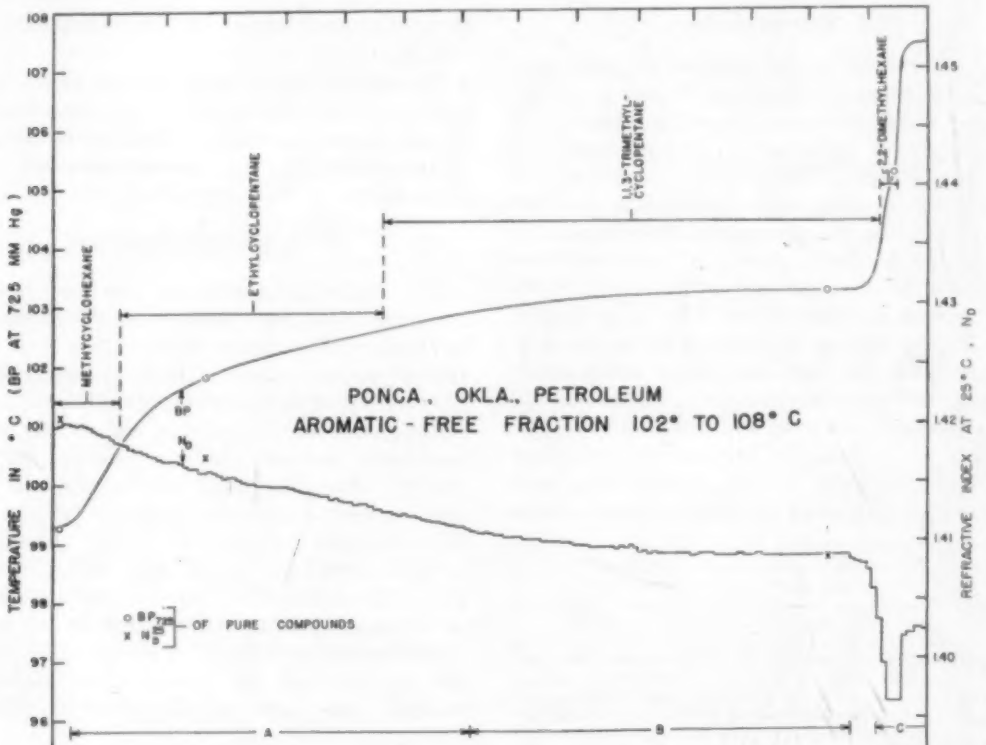

FIGURE 1.—*Distillation of the 102° to 108° C (aromatic-free) fraction of petroleum.*

The ordinate scale on the right gives the refractive indices of the fractions of distillate, and the ordinate scale on the left gives the boiling point of the distil at 725 mm. The scale of abscissas gives the volume of distillate in milliliters. The relative amounts by volume of the various components are indic in the upper portion of the figure.

sults of the distillation shown in figure 1. The nslation of these amounts into amounts based the entire gasoline fraction, 40° to 180° C, and the original crude petroleum was made from ublished data obtained in the investigation on hydrocarbons in the gasoline fraction of seven resentative crudes, which include the Ponca, kla., petroleum [12, 13, 14]. The data of this ter investigation [14] show that, for the Ponca, kla., naphtha, the material normally boiling in e range 102° to 108° C constitutes, by volume, percent of the gasoline fraction, 40° to 180° C, and 0.4$_7$ percent of the original crude petroleum.

IV. Results

Table 1 lists the several distillations that were performed in this investigation and gives information concerning the distillation column, the reflux ratio, the rate of collection of distillate, the azeotrope-forming substance (if used), the volume of hydrocarbon placed in the still, the volume of each fraction of distillate, and the number of the illustration in which the results of the distillation are plotted.

BLE 1.—*Information on the distillations for the analysis and separation of ethylcyclopentane, 1,1,3-trimethylcyclopentane, and 2,2-dimethylhexane from the 102° to 108° C (aromatic-free) fraction of petroleum*

Material	Distillation								
	Distilling column number	Number of theoretical plates at total reflux (approximately)	Reflux ratio (approximately)	Rate of collection of distillate	Kind of distillation	Volume of azeotrope-forming substance, if used	Volume of hydrocarbon charged	Volume of each fraction of distillate	Results plotted in figure
				ml/hr			*ml*	*ml*	
102° to 108° C (aromatic-free) fraction of petroleum.	2	100	120/1	2.5	Regular		1,650	7.5	1
Ethylcyclopentane concentrate (part *A*, fig. 1).	3	100	165/1	1.8	Azeotropic	Ethanol, 2,000 ml	530	14.0	2
Ethylcyclopentane concentrate (part *A*, fig. 2).	3	100	165/1	1.8	Regular		310	14.0	3
1,1,3-Trimethylcyclopentane concentrate (part *B*, fig. 1).	11A	200	180/1	4.0	Azeotropic	Isopropanol, 2,000 ml	500	16	4
2,2-Dimethylhexane concentrate (part *C*, fig. 1).	11A	200	180/1	4.0	do	Ethanol, 5,000 ml	1,950	16	5

Figure 1 shows the results of the distillation f that part of the petroleum containing all of the aterial (aromatic-free) normally boiling in the nge 102° to 108° C. The relative amounts of hylcyclopentane, 1,1,3-trimethylcyclopentane, d 2,2-dimethylhexane are marked in this art. It is possible that the relative amount of hylcyclopentane may be somewhat low because f the preferential loss of it in the previous treatent [8], which resulted in the separation of ethylcyclohexane. The relative amounts of e three compounds are given in the third colmn of table 2. Also given in table 2 are values presenting the amount of each of the compounds the gasoline fraction, 40° to 180° C, and the mount in the original crude petroleum [12, 13, 14].

Figure 2 gives the results of the azeotropic stillation with ethanol of the concentrate of hylcyclopentane, taken as part A in figure 1.

TABLE 2.—*Amounts of ethylcyclopentane, 1,1,3-trimethylcyclopentane, and 2,2-dimethylhexane in Ponca, Okla., petroleum*

Component	Normal boiling point	Relative amount by volume	Amount in the gasoline fraction, 40° to 180° C	Amount in the original crude petroleum
	°C		*Percent by volume*	*Percent by volume*
Ethylcyclopentane	103.5	34	0.4$_8$	0.1$_6$
1,1,3-Trimethylcyclopentane	104.9	64	.9$_1$	.3$_0$
2,2-Dimethylhexane	106.8	2	.03	.01
Total	-----	100	1.4$_2$	.4$_7$

Figure 3 gives the results of the regular distillation of the second concentrate of ethylcyclopentane, taken as part *A* in figure 2. The best lot from petroleum of ethylcyclopentane was selected from this distillate.

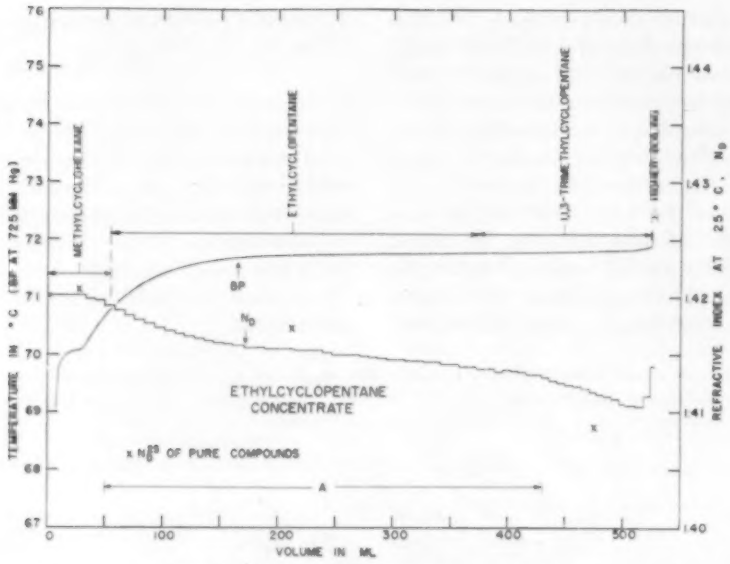

FIGURE 2.—*Distillation of the ethylcyclopentane concentrate (A, fig. 1).*

The ordinate scale on the right gives the refractive indices of the hydrocarbon portion of the fractions of azeotropic distillate, and the ordinate scale on the left gives the boiling point of the azeotropic distillate at 725 mm. The scale of abscissas gives the volume of the hydrocarbon portion of the distillate in milliliters. The relative amounts by volume of the various components are indicated in the upper portion of the figure.

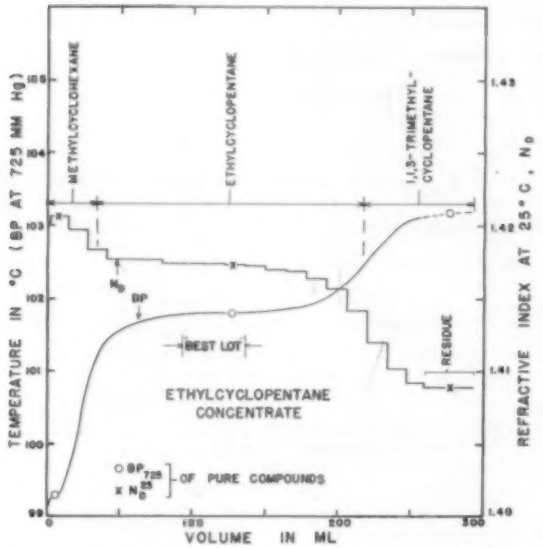

FIGURE 3.—*Distillation of the ethylcyclopentane concentrate (A, fig. 2).*

The ordinate scale on the right gives the refractive indices of the fractions of distillate, and the ordinate scale on the left gives the boiling point of the distillate at 725 mm. The scale of abscissas gives the volume of distillate in milliliters. The relative amounts by volume of the various components are indicated in the upper portion of the figure.

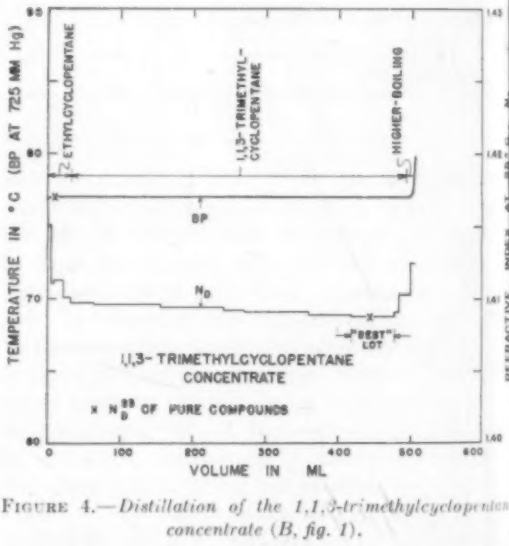

FIGURE 4.—*Distillation of the 1,1,3-trimethylcyclopentane concentrate (B, fig. 1).*

The ordinate scale on the right gives the refractive indices of the hydrocarbon portion of the fractions of azeotropic distillate and the ordinate scale on the left gives the boiling point of the azeotropic distillate at 725 mm. The scale of abscissas gives the volume of the hydrocarbon portion of the distillate in milliliters. The relative amounts by volume of the various components are indicated in the upper portion of the figure.

Figure 4 gives the results of the azeotropic distillation with isopropanol of the concentrate of 1,1,3-trimethylcyclopentane, taken as part B in figure 1. The best lot from petroleum of 1,1,3-trimethylcyclopentane was selected from this distillate.

Figure 5 gives the results of the azeotropic distillation with ethanol of the concentrate of 2,2-dimethylhexane. The best lot from petroleum of 2,2-dimethylhexane was taken as the small fraction *A* in figure 5. The small fraction *B* in figure 5 was used for the spectrographic analysis.

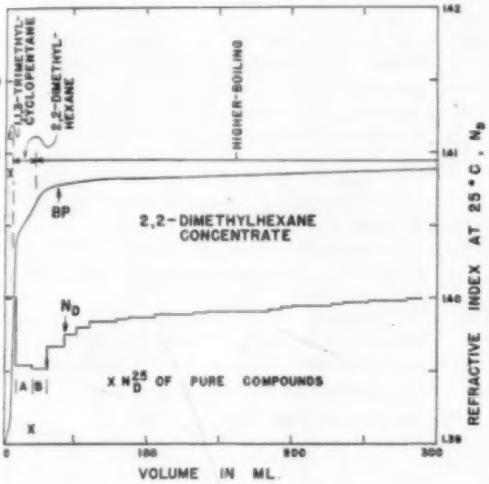

FIGURE 5.—*Distillation of the 2,2-dimethylhexane concentrate (C, fig. 1).*

The ordinate scale on the right gives the refractive indices of the hydrocarbon portion of the fractions of azeotropic distillate, and the ordinate scale on the left gives the boiling point of the azeotropic distillate at 725 mm. The scale of abscissas gives the volume of the hydrocarbon portion of the distillate in milliliters. The relative amounts by volume of the various components are indicated in the upper portion of the figure.

The values of the simple physical properties, and the calculated purity, for the best lots from petroleum of the two alkylcyclopentanes are given in table 3. The purities of the best lots from petroleum of ethylcyclopentane and 1,1,3-trimethylcyclopentane were calculated [15] from the freezing point, and the appropriate values of the cryoscopic constant and the freezing point for zero impurity [16], to be 98.13 and 98.06 mole percent, respectively. Within the indicated limits of uncertainty, and taking cognizance of the nearly 2 percent of impurity, the values of the simple physical properties of these samples from petroleum are in accord with the corresponding values for the API–NBS samples of the same compounds [17]. Both of the best lots from petroleum of these two compounds were analyzed spectrographically with an infrared spectometer by the Socony-Vacuum Laboratories [19], with the following results for the purity, in mole percent: Ethylcyclopentane, 98.5± 0.8; 1,1,3-trimethylcyclopentane, 99.0 ±0.8. These results are, within the respective limits of uncertainty, in good agreement with the values calculated from the measurements of freezing points.

TABLE 3.—*Values of the simple physical properties, and the calculated purity, for the "best lots from petroleum" of ethylcyclopentane and 1,1,3-trimethylcyclopentane*

Properties	Best lot from petroleum of ethylcyclopentane	Best lot from petroleum of 1,1,3-trimethylcyclopentane
Boiling point, at 760 mm, in ° C.	103.50 ±0.05	104.93 ±0.05.
Refractive index, N_D, at 25° C.	1.4174 ±0.0001	1.4088 ±0.0001.
Density,[a] in air at 1 atm, at 25° C, in g/ml.	0.7619 ±0.0001	0.7442 ±0.0001.
Freezing point,[b] in air at 1 atm, in ° C.	−139.06 ±0.02	−142.93 ±0.02.
Calculated purity,[c] mole percent.	98.13 ±0.15	98.06 ±0.35.

[a] Determined by A. F. Forziati with the apparatus described in reference [18].

[b] Determined by N. C. Krouskop, as described in reference [15].

[c] Calculated, as described in reference [15], from the value of the freezing point for zero impurity and the cryoscopic constant taken from reference [16].

Material *A* in figure 5 was selected, from the values of boiling point and refractive index, as the best lot from petroleum of 2,2-dimethylhexane. This lot, which was obviously not pure 2,2-dimethylhexane, had the following properties: Boiling point at 760 mm, 106.6±0.3° C; density at 25° C, 0.7045 g/ml; refractive index, n_D, at 25° C, 1.3954. The amount of 2,2-dimethylhexane in this lot was calculated to be 50 ±10 percent, from calculations made in three ways: (1) from the temperature-volume distillation data, (2) from the values of refractive index of the sample, of pure 2,2-dimethylhexane, and of the lower and higher-boiling components, and (3) from the values of refractivity intercept of the sample, of pure 2,2-dimethylhexane, and of the lower and higher-boiling components. A second and less pure lot of 2,2-dimethylhexane, *B* in

figure 5, was analyzed spectrographically with an infrared spectrometer [19] by the Socony-Vacuum Laboratories and found to contain somewhat over 20 percent of 2,2-dimethylhexane.[5]

Grateful acknowledgment is made to P. V. Keyser, Jr., and F. P. Hochgesang, Socony-Vacuum Laboratories, Paulsboro, N. J., for the spectrographic measurements reported in this paper.

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WASHINGTON, January 24, 1947.

[5] The lower refractive index of this lot is due to the increased concentration of higher-boiling paraffins.

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Heats of Combustion and Solution of Liquid Styrene and Solid Polystyrene, and the Heat of Polymerization of Styrene[1]

By Donald E. Roberts, William W. Walton, and Ralph S. Jessup

Bomb-calorimetric measurements have yielded for the heats of combustion ($-\Delta H_c^\circ$) at 25° C of liquid styrene and solid polystyrene to form gaseous carbon dioxide and liquid water the values 4394.88 ± 0.67 int. kj/mole (1050.58 ± 0.14 kcal/mole), and 4325.09 ± 0.42 int. kj/C_8H_8-unit (1033.89 ± 0.10 kcal/C_8H_8-unit), respectively, and for the heat of polymerization of liquid styrene to solid polystyrene at 25° C the value 69.79 ± 0.66 int. kj/mole (16.68 ± 0.16 kcal/mole). The results obtained on two samples of polystyrene of different molecular weight were in agreement within the precision of the measurements.

Measurements of the heat of solution of solid polystyrene in liquid monomeric styrene gave the value 3.59 ± 0.21 int. kj (0.86 ± 0.05 kcal) evolved per C_8H_8-unit of polystyrene at 25° C. Addition of this to the value for the heat of polymerization of liquid styrene to solid polystyrene gives the value 73.38 ± 0.69 int. kj (17.54 ± 0.16 kcal) per mole of styrene for the heat of polymerization of liquid styrene at 25° C, when the final product is a solution of polystyrene in styrene containing 6.9 percent by weight of polystyrene.

I. Introduction

The heat of polymerization of styrene can be obtained directly by measuring the heat evolved when the polymerization reaction is allowed to take place in a calorimeter, or it can be obtained indirectly as the difference between the heats of combustion of liquid monomer and solid polymer. In the direct measurement, the polymerization is not complete, as a rule, so that the heat evolved is that corresponding to a polymerization reaction in which the final product is a solution of polymer in monomer. The indirect determination, on the other hand, yields the heat of polymerization of the liquid monomer to solid polymer. In order to compare values of heat of polymerization obtained by the two methods it is necessary to have a value for the heat of solution of polymer in monomer.

Although the indirect determination has the disadvantage that the heat of polymerization is obtained as the small difference between two large quantities, the precision of bomb-calorimetric measurements is such that the accuracy of the indirect determination is comparable with that of direct determinations which have been reported [1, 2].[2] The indirect method has the advantage that the effect of the molecular weight of the product on the heat of polymerization can be investigated by using polymer fractions of widely different molecular weights.

The purpose of this paper is to present results of bomb-calorimetric measurements on styrene and on two samples of polystyrene having different average molecular weights, and a value of heat of polymerization derived therefrom. Data obtained in measurements of the integral heat of solution of polystyrene in liquid styrene, which can be

[1] Presented before the High Polymer Forum at the 110th meeting of the American Chemical Society, Chicago, Sept. 11, 1946. This paper also will appear in the J. Polymer Sci. 2, No. 3 (1947).

[2] Figures in brackets indicate the literature references at the end of this paper.

used to compare the results of the measurements reported here with values obtained by direct measurements of heat of polymerization made at this Bureau [1] are also given. In themselves, calorimetric determinations of partial molar heats of solution are of importance in connection with studies of thermodynamic properties of polymer solutions, and as the dependence of heat of solution upon concentration is not yet known, further work is contemplated.

II. Methods and Apparatus

In this work, measurements of heats of combustion of liquid monomer and solid polymer were made with the same bomb calorimetric system, and the difference in the results was taken as the heat of polymerization of liquid monomer to solid polymer. In calculating the results of the measurements of heat of combustion, the amount of the combustion reaction in each experiment was derived from the mass of carbon dioxide formed, using the value 44.010 for the molecular weight of carbon dioxide.

The calorimetric system was calibrated with Standard Sample 39f of benzoic acid, using the value reported previously [3] for the heat of combustion of this sample under the conditions of the bomb process.

The observed heat of combustion in each experiment was corrected for heat of stirring and heat transfer between calorimeter and surroundings, for energy used to ignite the charge, and for energy produced by formation of nitric acid in the bomb. In the experiments with polystyrene a small amount (0.14 to 0.36 mg) of unburned carbon was left in the crucible. Correction for this was applied both to the observed mass of carbon dioxide formed and to the observed heat of combustion using 33 int. kj/g as the heat of combustion of carbon.

The observed value of heat of combustion in each experiment was reduced, in accordance with the procedure described by Washburn [4], to the value of $-\Delta U_c^\circ$ (25° C), the decrease in intrinsic energy accompanying the combustion reaction

$$C_8H_8+10O_2(g)\rightarrow 8CO_2(g)+4H_2O(liq)$$

with each of the reactants and products in its thermodynamic standard state. The standard state for C_8H_8 in this equation is that of the liquid monomer or solid polymer at 25° C and a pressure of 1 atmosphere.

The heat evolved at 25° C in the polymerization reaction per mole of monomer $-\Delta U_P^\circ(=-\Delta H_P^\circ$ was then calculated by means of the relation $-\Delta U_P^\circ=(-\Delta U_c^\circ)_m-(-\Delta U_c^\circ)_p$, where the subscripts m and p refer to liquid monomer and solid polymer, respectively.

The samples of polystyrene, which were fine powders, were compressed into pellets and then weighed in the platinum crucible in which they were to be burned. The samples of liquid styrene were enclosed in thin-walled glass bulbs [5, 6] which were flattened on opposite sides and filled completely with the liquid. The method described in the references cited for filling such bulbs consisted in immersing the end of the stem in the liquid, and then alternately heating the bulb to expel air, and allowing it to cool and draw in liquid. As it was thought undesirable to heat the styrene, a different method of filling the bulbs was used. This method consisted in immersing the end of the stem in the liquid, and then alternately applying pressure gently with the fingers to the flat sides of the bulb to expel air, and releasing the pressure. The weight of glass in each bulb after removing the stems was about 0.05 g.

The apparatus and procedure followed in the bomb-calorimetric measurements have been described previously [7, 8, 9]. The bomb used is made of illium and is similar in design to that described by Prosen and Rossini [10]. The bomb had a capacity of 380 ml. One milliliter of water was placed in the bomb before each combustion experiment. The carbon dioxide formed in combustion was absorbed in Ascarite and weighed, following the procedure described by Rossini [11]. The absorption train used was similar to that described in reference [10], but no provision was made for oxidizing products of incomplete combustion and absorbing the resulting carbon dioxide. However, frequent tests for carbon monoxide in the gaseous products of combustion were made, using an NBS colorimetric method [12], but no carbon monoxide was ever found.

The heat of solution of polystyrene in liquid styrene was determined by observing the temperature rise of the calorimeter produced by the solution of about 1 g of polystyrene in 15.0 ml of styrene.

The calorimetric apparatus used in the measurements of the heat of solution was the same as that used in the combustion experiments, except that the calorimeter cover was omitted, and a straight glass tube about 300 mm in length by 11.5 mm inside diameter was used to contain the sample of liquid styrene. This tube was immersed to a depth of 225 mm in the water of the calorimeter and extended about 40 mm above the jacket. The finely powdered sample of polystyrene was contained in a cylinder 10 mm in diamter and 110 mm long made of 200-mesh copper gauze, which was placed in the glass tube above the surface of the liquid styrene, and was suspended by a thin-walled copper-nickel tube. The temperatures of the calorimeter and jacket were both brought near to 30° C, with the temperature of the jacket slightly higher than that of the calorimeter, so that there was a small positive rate of change of calorimeter temperature due to thermal leakage. After a wait of several minutes for the attainment of a steady positive rate, a series of observations of calorimeter temperature and corresponding time was made over a period of 10 minutes. The copper-gauze cylinder containing the sample of polystyrene was then lowered into the styrene and moved up and down by hand once a second to stir the liquid. The temperature of the calorimeter rose rapidly at first, but the rate of rise decreased with time and attained a small constant value after about 10 minutes, indicating that solution of the polystyrene was complete. Stirring of the solution was continued for 10 more minutes, and readings of time and temperature were continued for 10 minutes after the stirring was stopped. The rate of change of calorimeter temperature decreased slightly when the stirring was stopped. This was attributed to a combination of heat of stirring of the viscous solution, and conduction of heat to the calorimeter from the hands during the stirring. Correction to the observed temperature rise during the "reaction period" was made for these effects, and for heat transfer between calorimeter and jacket.

The energy unit used in the original calculation of the results is the international joule. Conversion to the conventional thermochemical calorie was made by the relation [13] 1 calorie=4.1833 int. j.

III. Materials

The samples of styrene and polystyrene used in the bomb-calorimetric measurements were obtained from the Dow Chemical Co. The styrene was a selected sample, and was purified at this Bureau [3] by passing it through silica gel, by three fractional freezings, and by distillation in vacuum. Freezing curves indicated a purity of the final product of 99.95 mole percent. Mass spectrographic analysis [4] indicated a composition of 99.91 mole percent styrene and 0.09 mole percent ethylbenzene. The observed bomb-calorimetric data on styrene were corrected for the presence of this amount of ethylbenzene by using the heat of combustion data reported by Prosen, Gilmont, and Rossini [14].

After purifiying the sample it was stored in an evacuated sealed glass container at the temperature of dry ice until time for making the calorimetric measurements. It was then warmed to room temperature, a sample was transferred to a glass bottle, and 10 ppm of tertiary butyl catechol was added to this sample to inhibit polymerization. The calorimetric measurements on the monomer were completed within 1 month after it was warmed to room temperature.

The two samples of polystyrene obtained for the bomb-calorimetric measurements, samples I and II, were commercial unfractionated polymers, containing about 3 percent of methanol-soluble material (partly low-molecular-weight polymer and unpolymerized styrene). The monomer used was 99.7 percent styrene, and most of the impurity was ethylbenzene. Each sample was prepared by thermal polymerization without catalysts at a range of temperatures, the average for the two samples being of the order of 100° C and above, and may have had a wide range of molecular weights present. However, precipitation tests [5] showed that as methanol was slowly added to a toluene solution of the polymer, a large fraction of the material was precipitated over a narrow range of added precipitant, indicating that a large portion of each polymer probably was of nearly uniform molecular weight.

[3] The purification and testing for purity by observation of freezing behavior were done by members of the staff of the low-temperature laboratory at the Bureau.

[4] By A. K. Brewer.

[5] By I. C. Schoonover of the Bureau.

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The sample of polystyrene used in the measurements of heat of solution, sample III, was obtained from Monsanto Chemical Co. It was a commercial material designated as type *A*, and was prepared in the form of a fine powder by solution in toluene and precipitation with methanol in the manner described below for samples I and II.

The styrene used in heat of solution measurements was a technical sample obtained from Dow Chemical of Canada, Ltd. Freezing curves indicated that it was 99.8 mole percent styrene, the most likely impurities being ethylbenzene and polystyrene.

A few preliminary bomb-calorimetric measurements were made on samples I and II of polystyrene without purification, except for removal of visible particles of foreign material. The remainder of each of these samples was purified at this Bureau, by the method of I. C. Schoonover, which produces a fine powder rather than a gel. According to this procedure, 20g of the material was dissolved in 2½ liters of chemically pure filtered and distilled toluene by allowing the mixture to stand for 24 hr, with intermittent shaking. The solution was filtered through a fine sintered glass funnel. Two hundred milliliters of the filtered solution was slowly added to 3 liters of chemically pure methanol in a 4-liter Erlenmeyer flask, with continuous stirring. Stirring was continued for ½ hr after all of the toluene solution had been added and the precipitate was then allowed to settle overnight.

The supernatant liquid was decanted, the precipitate collected upon a large sintered-glass funnel, and washed eight times with methanol.

When the entire amount of polystyrene solution had been treated in this manner, the precipitates were then dried for 18 hr in a thin layer at 70° C under a pressure of about 75 mm of mercury. The dried material was ground, mixed, and dried for an additional 72 hr under the same conditions with intermittent stirring to expose fresh surfaces. A test made by moistening the dried material with methanol and drying again indicated that the material probably did not retain methanol under these conditions of drying.

It is believed that the above treatment removed most of any monomer and low-molecular-weight polymer that may have been present. It was found, however, that the polymer increased in weight by about 0.1 percent during the drying process. One sample (not used for combustion measurements) that was kept for about 1 month under the above conditions of drying increased in weight by about 1 percent. Within the limits of precision of the measurements, the heats of combustion of the purified and unpurified samples per gram of carbon dioxide formed were the same. The heat of combustion of the purified material per gram of sample burned was found to be about 0.06 percent less than that of the unpurified material. These facts suggest that the removal of monomer and low molecular-weight polymer in the purification process did not affect the heat of combustion per gram of carbon dioxide formed by a measurable amount, and that the increase in weight of the material during drying was due to the absorption of gas, which behaved as an inert impurity.

The three samples of polystyrene were characterized, after purification, by viscosity determinations. Measurements were made with an Ostwald (Fenske type 50) viscometer at a temperature of 30.50° ± 0.05° C. The viscometer was calibrated with water, and it was found that the kinetic-energy correction to the viscosity was negligible over the range of viscosities measured on the polystyrene samples. The viscosities of the polystyrene samples were measured in toluene solutions at concentrations of 1, 0.5, 0.25, and in some cases, 0.125 g/100 ml of solution. The results were plotted by the method of Huggins [15], and the following values obtained for the intrinsic viscosity $[\eta]$ and the constant k' in the Huggins [6] equation:

	$[\eta]$	k'
Sample I	1.650	0.206
Sample II	0.791	.232
Sample III	1.255	.217

These data indicate that samples I and II, used in the bomb-calorimetric measurements, differed considerably in average molecular weight (sample I having about twice the molecular weight of sample II) and that the degree of polymerization

[6] $\eta_{sp}/c=[\eta]+k'[\eta]\eta_{sp}$, where c is the concentration in grams per 100 ml of solution, η_{sp} is specific viscosity, and k' is a constant that determines the dependence of the viscosity on concentration and depends on the type of polymer, on the solvent and on the temperature, but is supposed to depend only slightly, or not at all, on the molecular weight of the polymer.

of sample III, used in the measurements of heat of solution was intermediate between those of samples I and II. It may be noted that there are not very wide differences among the values of k'.

IV. Results

The results of the calibration experiments are given in table 1. Because of slight changes in the calorimetric system resulting from repairs to the bomb, and the substitution of a new resistance thermometer for the one used initially, several series of calibration experiments were made during the course of the work. These are designated by the letters *A*, *B*, *C*, in table 1.

TABLE 1.—*Results of calibration of calorimeter with benzoic acid*

Observed energy equivalent at 28.5° C for series—		
A	*B*	*C*
Int. j/° C	*Int. j/° C*	*Int. j/° C*
13828.0	13825.9	13826.9
13823.6	13827.1	13821.9
13828.6	13829.9	13822.6
13826.0	13828.2	13827.4
13827.3	13823.3	13835.0
13823.9	13825.3	13832.5
13825.2	13829.5	13829.0
13818.8	13822.4	13826.4
13825.7	13822.6	13822.9
13827.0	13822.8	13823.8
13824.8	13818.2	13825.5
	13817.7	
Mean 13825.4±0.8 [a]	13823.2	Mean 13826.7±1.2 [a]
	13828.7	
	13824.0	
	13824.3	
	Mean 13824.6±0.9 [a]	

[a] See footnote 7, page 632.

The results of measurements of heat of combustion are given in table 2, where $-\Delta U_B$ is the observed heat of combustion in the bomb under the conditions specified in columns 2 and 3 of the table, and $-\Delta U_c^\circ$ represents the decrease in intrinsic energy accompanying the combustion reaction when the reactants (liquid styrene or solid polystyrene and gaseous oxygen) and products (gaseous carbon dioxide and liquid water) are all in their thermodynamic standard states. The letters *A*, *B*, *C*, following the material names in table 2 indicate the series of calibration experiments listed in table 1, upon which the results are based.

TABLE 2.—*Results of bomb-calorimetric measurements on polystyrene and styrene*

Mass of sample	Initial O_2 pressure, 30° C	Mass of CO_2	Heat of combustion at 30° C	
			$-\Delta U_B$	$-\Delta U_c^\circ$
POLYSTYRENE I (*A*) [a]				
g	*atm*	*g*	*Int. j/g* CO_2	*Int. j/g* CO_2
1.04199	35.9	3.51789	12273.0	12265.5
0.83779	35.8	2.82821	12276.5	12269.4
.89085	35.7	3.00708	12275.3	12268.1
.87126	35.7	2.94205	12273.2	12266.0
.84294	35.7	2.84516	12273.6	12266.5
.70051	35.8	2.36437	12276.5	12269.6
Mean				12267.5
Standard deviation of mean [b]				±1.3
POLYSTYRENE II (*B*) [a]				
0.54714	35.8	1.84806	12279.1	12272.4
.99097	35.8	3.34687	12274.3	12267.0
.97718	35.8	3.29996	12273.4	12266.1
.98993	35.8	3.34174	12273.5	12266.2
.96938	36.0	3.27295	12275.3	12268.0
Mean				12267.9
Standard deviation of mean [b]				±1.6
Weighted mean for polystyrene				12267.6
Standard deviation of weighted mean [b]				±1.2
STYRENE (*C*) [a]				
1.17387	32.5	3.96699	12474.1	[c] 12466.6
0.77992	32.6	2.63602	12478.0	12471.1
.79241	32.3	2.67778	12478.7	12471.8
.73714	32.8	2.49141	12473.7	12466.8
.86098	32.8	2.91015	12469.4	12462.3
.72861	32.7	2.46261	12471.6	12464.8
.78500	32.8	2.65316	12469.7	12462.7
Mean				12466.6
Standard deviation of mean [b]				±1.9

[a] See preceding column for an explanation of the significance of the letters *A*, *B*, and C.

[b] Each value of standard deviation of the mean was calculated from the data of the experiments with the styrene or polystyrene sample and the corresponding experiments with benzoic acid, in the manner described in footnote 7, page 632.

[c] The values of $-\Delta U_c^\circ$ for styrene were derived from the corresponding values of $-\Delta U_B$ by applying the Washburn correction and a correction of 34 ppm for the ethylbenzene in the sample.

The values obtained for the mass of carbon dioxide formed in combustion, which is a measure of the amount of reaction, are lower than the corresponding values calculated stoichiometrically from the masses of samples burned, assuming that the composition of the samples is represented by $(C_8H_8)_x$. The average differences between observed and calculated masses of carbon dioxide

are, for styrene, 0.029 percent, and for the samples of polystyrene I and II, respectively, 0.146 and 0.115 percent. Frequent measurements of the carbon dioxide formed in combustion of Standard Sample 39f of benzoic acid yielded results in agreement with calculated values within less than 0.01 percent on the average. The observed deficiency of carbon dioxide in the case of styrene can probably be attributed to air or moisture dissolved in the liquid. The deficiency in the case of the samples of polystyrene is probably due to the presence of nonhydrocarbon material in the samples as an impurity.

It will be seen from the data of table 2 that the values of $-\Delta U_c°$ for the two samples of polystyrene are practically identical, even though the indicated amounts of impurity were different. This suggests that a part of the nonhydrocarbon content of the samples behaved simply as an inert impurity, but as the combined uncertainties of the calorimetric results, and of the measurements of the carbon dioxide formed are of the same order of magnitude as the difference in indicated impurity in the two samples, no definite conclusion can be drawn as to this point. It is here assumed that the nonhydrocarbon content of the polystyrene samples is entirely inert impurity.

The data in table 2 then indicate that the heat of combustion of polystyrene per gram of carbon dioxide formed is independent of molecular weight, at least over the range of the material studied. The weighted mean of the values for the two samples is therefore taken as the value derived from the present measurements for the heat of combustion of polystyrene.

In table 3 are given values of heat of combustion per mole (or per C_8H_8-unit) for styrene and polystyrene, calculated from the mean values given in table 2. In reducing the values at 30° to 25°C, use was made of unpublished data obtained at the Bureau on the heat capacities of polystyrene and styrene [16]. The values of heat capacities were 128.48 int. j/C_8H_8-unit degree and 182.20 int. j/mole degree at 27.5° C for polystyrene and styrene, respectively.

The value derived from the data given in table 3 for the heat of polymerization of liquid styrene to solid polystyrene at 25° C, that is, the difference between the values for heats of combustion of monomer and polymer is $-\Delta H_P(25° C) = 69.79 \pm 0.66$ int.kj,[7] or 16.68 ± 0.16 kcal/mole of monomer.

The data obtained in measurements of the integral heat of solution of polystyrene in styrene are given in table 4. The values given represent the heat evolved when polystyrene is dissolved in styrene to form a solution containing an average of 6.9 percent by weight of polystyrene. The average concentration of polymer in the resulting solution was about the same as the concentration of polymer in the final solution obtained in the direct measurements of heat of polymerization [1] made at the Bureau.

TABLE 3.—*Values of heat of combustion*

	Polystyrene (solid)	Styrene (liquid)
$-\Delta U_c°(30° C)$	4319.18 ±0.42 int. kj/C_8H_8-unit.[a]	4389. 24±0.67 int. kj/mole.[a]
	1032.48 ±0.10 kcal/C_8H_8-unit.	1049.23 ±0.14 kcal/mole.
$-\Delta H_c°(30° C)$	4324.22 ±0.42 int. kj/C_8H_8-unit.	4394.28 ±0.67 int. kj/mole.
	1033.69 ±0.10 kcal/C_8H_8-unit.	1050.43 ±0.14 kcal/mole.
$-\Delta U_c°(25° C)$	4320.13 ±0.42 int. kj/C_8H_8-unit.	4389.92 ±0.67 int. kj/mole.
	1032.71 ±0.10 kcal/C_8H_8-unit.	1049.39 ±0.14 kcal/mole.
$-\Delta H_c°(25° C)$	4325.09 ±0.42 int. kj/C_8H_8-unit.	4394.88 ±0.67 int. kj/mole.
	1033.80 ±0.10 kcal/C_8H_8-unit.	1050.58 ±0.14 kcal/mole.

[a] See footnote 7.

[7] Except where otherwise noted, the number following each ± sign is a measure of the precision of the result which is defined as follows: In the case of a value of heat of combustion, the measure of precision is taken as [17]

$$s = Q\sqrt{(s_E/E)^2+(s_Q/Q)^2+(s_B/B)^2+(s_H/H)^2}$$

In this expression, s_E is the standard deviation of the mean of the results of the series of experiments with benzoic acid to determine E, the energy equivalent of the calorimetric system; s_Q is the standard deviation of the mean of the results of the series of experiments to determine Q, the heat of combustion of the sample; (s_B/B) is an allowance of 5×10^{-5} for the standard deviation of the value used for the heat of combustion of benzoic acid; and (s_H/H) is an allowance of 5×10^{-5} for the standard deviation associated with the determination of the amount of the combustion reaction from the mass of carbon dioxide formed. The corresponding measure of precision of the value of heat of polymerization is defined as

$$s' = \sqrt{(s_m')^2+(s_p')^2}$$

In this expression s_m' and s_p' were calculated from the data of the heat of combustion measurements on monomer and polymer, respectively, by means of expressions of the form

$$s_m' = Q\sqrt{(s_E/E)^2+(s_Q/Q)^2}$$

Here it is assumed that systematic errors in the value used for the heat of combustion of benzoic acid and in the method of determining the amount of the combustion reaction will cancel in taking the difference between the heats of combustion of polymer and monomer.

"Standard deviation of the mean" as used above is defined as $(1/\sqrt{n})\times\sqrt{\Sigma d^2/n}$, where d is the difference between a single observation and the mean, and n is the number of observations.

TABLE 4.—*Results of measurements of the heat of solution of polystyrene in styrene*

Mass of polystyrene [a]	Observed heat of solution ($-\Delta H$, 25° C)	
	Int. kj/C_8H_8-unit	kcal/C_8H_8-unit
g		
0.897	3.99	0.95
0.908	3.58	.86
0.986	2.91	.69
1.106	3.88	.93
Mean 0.997	3.59	0.86
Standard deviation of mean	±0.21	±0.05

[a] Dissolved in 15.0 ml of styrene.

These measurements of heat of solution are believed to be the only ones reported for a solution of polymer in its own monomer. The observed evolution of heat reported in this paper has been surprising to some persons with whom this work has been discussed.

It was expected that the heat of solution would be quite small considering the chemical similarity of the two materials. Flory [18] assumes that the heat of mixing of polystyrene and toluene is negligible, but Schulz [19] found an evolution of heat upon dissolving polystyrene in benzene. It may be noted that heat is evolved when cellulose derivatives are dissolved in various solvents [20, 21, 22, 23, 24, 25]; heat is absorbed in rubber-solvent systems [26, 27, 28] and the heat effect is zero with gutta-percha and toluene [29].[8] The fact that heat is evolved suggests that the attractive force between adjacent polymer molecules is less than that between polymer and monomer molecules.

Addition of the value 69.79±0.66 int. kj or 16.68±0.16 kcal/mole for heat of polymerization of liquid monomer to solid polymer to the value 3.59±0.21 int. kj/C_8H_8-unit, or 0.86±0.05 kcal/C_8H_8-unit given in table 4 for the heat of solution of solid polystyrene in liquid styrene yields the value 73.38±0.69 int. kj or 17.54±0.16 kcal/mole of monomer for the heat of polymerization of liquid styrene at 25°C when the final product is a solution of polystyrene in liquid styrene. It would have been more satisfactory if the same sample of polystyrene could have been used in both the combustion and the solution measurements. However, it is thought that the branching, ring formation, or other differences that have been ascribed [30] to different conditions of polymerization probably would not have an effect greater than experimental error on the thermal values reported here. It will be noted that there is good agreement with the heat of polymerization as measured directly [1].

For convenient reference, a recapitulation of the essential numerical results obtained is as follows:

	$-\Delta H°_{298.16}$
Heat of combustion:	
Monomer	1050.58 kcal/mole.
Polymer	1033.89 kcal/C_8H_8-unit.
Heat of solution of polymer in monomer	0.86 kcal/C_8H_8-unit.
Heat of polymerization to:	
Solid polymer	16.68 kcal/mole.
Solution	17.54 kcal/mole.

V. Discussion

The method that has been used for calculating heat of polymerization from bomb-calorimetric data is based on the assumption that the polymerization reaction is represented by

$$x\mathrm{C_8H_8(liq)} \rightarrow (\mathrm{C_8H_8})_x\mathrm{(solid)} \qquad (1)$$

This equation may be more appropriately written in the form

$$x\mathrm{CH_2{=}CHC_6H_5} \rightarrow \mathrm{CH_3\text{-}CHC_6H_5\text{-}(CH_2\text{-}CHC_6H_5)_{x-2}\text{-}CH{=}CHC_6H_5} \qquad (2)$$

The double bond could conceivably be located in other parts of the chain, or as suggested by Risi and Gauvin [31] it could be destroyed by cyclization of the terminal linkages with the production of a molecule having an indane ring at the end:

$$\mathrm{CH_3\text{-}CHC_6H_5\text{-}(CH_2\text{-}CHC_6H_5)_{x-3}\text{-}CH_2\text{-}CH}\begin{matrix}\diagup\ \mathrm{CH^2}\ \diagdown\\ \\ \diagdown\ \mathrm{C_3H_4}\ \diagup\end{matrix}\mathrm{CH\text{-}C_6H_5} \qquad (3)$$

[8] References numbered [19, 21, 22, 23, 24, 25 and 28] are to work in which the heat was measured calorimetrically. In references [20, 26, 27, and 29] the heat effect was calculated from osmotic- or vapor-pressure measurements.

According to information supplied by the Dow Chemical Co., polystyrene samples I and II were prepared by straight thermal polymerization of styrene, which was at least 99.7 percent pure. The impurity was mostly ethylbenzene, with approximately 100 ppm of some organic peroxide. It therefore seems unlikely that the composition of the polymer molecules differed from that indicated by the formula $(C_8H_8)_x$ by amounts sufficient to affect the heat of combustion of the polymer by a significant amount. In particular, the presence of fragments of catalyst or solvent molecules on the ends of the polymer chains [32, 33, 34, 35, 36, 37] seems extremely unlikely.

As noted previously, the amount of carbon dioxide formed in the combustion of the polystyrene samples was less than that calculated from the mass of sample burned. The fact that the amount of nonhydrocarbon impurity indicated by the deficiency of carbon dioxide is about the same as the increase in weight of the polymer samples during drying makes it appear likely that the nonhydrocarbon impurity was largely gas absorbed during drying. If this gas was oxygen that reacted chemically to become a part of the polymer molecules, the heat of combustion of the polymers per gram of carbon dioxide formed would be lower than that of a polymer having the composition $(C_8H_8)_x$, and the value derived from the heat of combustion data for the heat of polymerization according to reaction 1 would be correspondingly too high. Making reasonable assumptions as to the molecular weights of the polymers, it is estimated that 0.15 percent by weight of oxygen chemically combined with sample I of polystyrene would lower its heat of combustion per gram of carbon dioxide by an amount corresponding to an increase of about 3 percent of the heat of polymerization. The corresponding effect of 0.11 percent combined oxygen in the case of polystyrene sample II would be of the order of 2 percent of the heat of polymerization. As noted previously, however, the experimental data on heats of combustion indicate that the gas absorbed by the polymer in drying did not combine chemically with it, but behaved simply as an inert impurity.

VI. Previous Work

Measurements of the heats of combustion of styrene and two samples of polystyrene have been reported by Luschinsky [38]. One of his samples of polystyrene (sample *A*) was prepared by polymerizing styrene for 6 hr. at 180° C, dissolving the product in toluene and distilling off the toluene and any remaining monomer in vacuum, and then redissolving the product in toluene and drying in high vacuum at 100° C. His other sample (sample *B*) was obtained by fractionating a part of sample *A* by precipitation from solution in methyl ethyl ketone in such a manner that a sample having a narrow range of molecular weights was obtained.

Measurements of heat of combustion were made by means of a bomb calorimeter. The method used to prevent evaporation of styrene was probably not completely effective. The amount of reaction in each case was determined from the mass of sample burned.

The values reported for heat of combustion of styrene, polystyrene *A*, and polystyrene *B* are 1045.4, 1034.8, and 1031.6 kcal/mole of monomer, respectively. Certain small corrections would have to be applied to these values to convert them to the same basis as the values of heat of combustion reported in this paper, but as these corrections would be substantially the same for styrene, and for the two samples of polystyrene, the resulting values for heat of polymerization will not be affected by omission of these corrections. The values of heat of polymerization of styrene to solid polystyrene derived from Luschinsky's data are 10.6 and 13.8 kcal/mole of monomer for polystyrene samples *A* and *B*, respectively.

Prosen, Gilmont, and Rossini [14] have reported the value 1050.40 ±0.20kcal/mole for the heat of combustion, $-\Delta H_c°$, of liquid styrene at 25° C. This value is in agreement within 0.017 percent with that derived from the results presented in this paper. Further references to earlier work will be found in reference [14].

Schulz [19] has made measurements of the integral heat of solution of polystyrene in benzene and has reported an evolution of 415 to 445 cal/C_8H_8-unit, the concentration of the solution being 3.3 percent by weight. This evolution of heat is only about half of that obtained in the work reported in this paper in which styrene was the solvent, and the concentration was 6.9 percent.

Votinov, Kobeko, and Marei [39] derived the

value 23 kcal/mole for the heat of depolymerization of polystyrene from the difference in activation energies of polymerization and depolymerization. They also reported, without experimental details, the values 9,831 and 10,041 cal/g (1023.8 and 1045.7 kcal/mole of monomer) for the heats of combustion of polymer and monomer, respectively, and 21.9 kcal/mole for the heat of polymerization of styrene derived from the values of heat of combustion.

Stanley [40] reported the value 20 kcal/mole of monomer for the heat of polymerization in styrene solution. The source of this figure was not given.

Direct measurements of the heat evolved during polymerization of styrene were made by Goldfinger, Josefowitz, and Mark [2]. They reported the value 15.0 kcal/mole of monomer for the heat of polymerization, at 70° to 140° C, the final product being a solution in which the monomer was 35 to 85 percent polymerized.

Direct measurements [1] of the heat of polymerization of styrene made at the low temperature laboratory of the Bureau have produced the result 17.8 kcal/mole of monomer, which is in good agreement with the corresponding value 17.54 kcal/mole of monomer reported in this paper.

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Torsion of a Rubber Cylinder

By Ronald S. Rivlin *

It has been predicted theoretically that, in general, a right-circular cylinder of incompressible, highly elastic material, which is isotropic in its undeformed state, cannot be held in a state of pure torsional deformation by means of a torsional couple alone. In addition, normal surface tractions must be exerted over the plane ends of the cylinder. These normal surface tractions depend on the amount of torsion and on position on the plane ends of the cylinder. Experiments are reported here in which this phenomenon is observed in a right-circular cylinder of pure gum compound. The dependence of the surface traction on amount of torsion and its distribution over the surface of the cylinder is studied by measuring the bulging of the rubber into small holes in a metal plate on one end of the cylinder.

I. Introduction

In a series of papers that is pending publication elsewhere,[1] the mechanical properties of highly elastic materials, such as rubber, which can be assumed incompressible and isotropic in their undeformed state, are discussed in terms of a stored-energy function, W. This stored-energy function is specified in terms of the invariants of strain. It is shown that, once W is specified in this manner, the forces, which must be applied in order to support any given state of deformation, can be calculated. This calculation has been carried out for the pure torsional deformation of a right-circular cylinder, for an assumed stored-energy function of simplest possible type and subsequently for any general form of stored-energy function.

The theory predicts that in order to produce a pure torsion in the cylinder, a torsional couple must be exerted on the plane ends of the cylinder, as in the classical theory of elasticity for small deformations. In addition, normal tractions must be exerted over these surfaces. The distribution of these normal tractions over the ends of the cylinder and their dependence on the amount of torsion have been calculated for any specified form of the stored-energy function.

In this paper experiments are reported in which this distribution and dependence on amount of torsion is measured for a cylinder of pure-gum compound, on the assumption that the surface traction is measurable by the bulging of the rubber into small holes in a metal plate on one end of the cylinder. The results obtained are compared with those derived theoretically for two simple forms of the assumed stored-energy function. Agreement, within the accuracy of the experiments, is obtained if the stored-energy function has a form equivalent to that put forward for rubber by Mooney.[2] This form involves two physical constants for the material.

II. Specification of the Stored-Energy Function

The stored-energy function for an ideal perfectly elastic material may be completely defined in the following manner. If a cube of the material, of unit edge, is subjected to a pure, homogenous deformation in which it is deformed into a cuboid

*Guest worker at the National Bureau of Standards, representing the British Rubber Producers' Research Association, Welwyn Garden City Herts., England.

[1] R. S. Rivlin, Phil. Trans. Roy. Soc. [A] (pending publication).

[2] M. Mooney, J. Applied Phys. **11**, 582 (1940).

of dimensions λ_1 by λ_2 by λ_3, then the strain invariants I_1, I_2, and I_3 are defined as

$$\left.\begin{aligned} I_1&=\lambda_1^2+\lambda_2^2+\lambda_3^2,\\ I_2&=\lambda_2^2\lambda_3^2+\lambda_3^2\lambda_1^2+\lambda_1^2\lambda_2^2,\\ I_3&=\lambda_1^2\lambda_2^2\lambda_3^2. \end{aligned}\right\} \quad (1)$$

If the material is isotropic in its undeformed state, the energy stored in the deformed cube is defined as the stored-energy function for the material. It must be a function of I_1, I_2, and I_3, provided it depends only on the state of deformation of the cube and not on the manner in which the deformation is reached. Once the form of this function is specified, the mechanical properties of any body of this material are, in principle, completely determinate and are purely a matter for calculation, provided such phenomena as internal friction and creep are negligible.

For an incompressible material, the volume of the cube considered is unaltered in the deformation, so that

$$I_3=\lambda_1^2\lambda_2^2\lambda_3^2=1 \quad (2)$$

Then W, the stored-energy function, is given by

$$W=W(I_1,I_2). \quad (3)$$

In general, the form of the function $W(I_1, I_2)$ will be such that when the body is undeformed $W=0$.

III. Torsion of a Right-Circular Cylinder

Let us consider a right-circular cylinder of radius, a, and length, l, of incompressible material, for which the stored-energy function, W, is given by eq 3. It has been shown that, in such a body, a pure torsion, in which each circular cross section of the cylinder is turned in its own plane through an angle $\phi(=\psi z)$ proportional to its distance z from one end, can be maintained by the application of surface tractions alone. The necessary system of surface tractions is indeterminate to the extent of an arbitrary hydrostatic pressure, but if the surface tractions applied to the curved surface of the cylinder are zero, then the surface tractions that must be applied to the plane ends have been calculated as (1) tangential surface tractions, Θ, acting azimuthally in the deformed state of the cylinder (these effectively act as a torsional couple on the cylinder), and (2) normal surface tractions, Z.

Θ and Z are measured per unit area of the surfaces on which they act and their distribution over the plane ends of the cylinder and dependence on Ψ are given by

$$\Theta=2\psi r\left(\frac{\partial W}{\partial I_1}+\frac{\partial W}{\partial I_2}\right)$$

and

$$Z=-2\psi^2a^2\left(\frac{\partial W}{\partial I_2}\right)_{r=a}+2\psi^2\int_a^r r\left[\left(\frac{\partial W}{\partial I_1}-2\frac{\partial W}{\partial I_2}\right)-2\left[\frac{\partial^2 W}{\partial I_1^2}+(3+\psi^2r^2)\left(\frac{\partial^2 W}{\partial I_1\partial I_2}\right)+(2+\psi^2r^2)\frac{\partial^2 W}{\partial I_2^2}\right]\right]dr+2\left[\frac{\partial W}{\partial I_1}-\left(\frac{\partial W}{\partial I_1}\right)_{r=a}\right]+4\left[\frac{\partial W}{\partial I_2}-\left(\frac{\partial W}{\partial I_2}\right)_{r=a}\right]. \quad (4)$$

in which r is the distance of the point considered from the axis of the cylinder. $\partial W/\partial I_1$, $\partial W/\partial I_2$, $\partial^2 W/\partial I_1^2$, etc. are, in general, functions of I_1 and I_2, which can be calculated if the form of $W(I_1, I_2)$ is known. For the deformation considered

$$I_1=I_2=3+\psi^2r^2 \quad (5)$$

We shall consider here two particular choices of the form of the stored-energy function, W, for which eq 4 are considerably simplified.

In the series of papers (see footnote 1) mentioned above, particular attention was paid to the stored-energy function given by

$$W=C_1(I_1-3), \quad (6)$$

when C_1 is a physical constant characterizing the material. Materials for which eq 6 are valid were described as incompressible, neo-Hookean materials.

The particular interest residing in this choice of the stored-energy function rests on the fact that (1) it is the simplest choice that can be made from the point of view of the formulation of a theory of large elastic deformations; (2) it is the form derived by Treloar,[3] for an ideal rubber, on the basis of the kinetic theory of large elastic deformations.

Equation 6 is a particular form, obtained by making $C_2=0$, of the relation

$$W=C_1(I_1-3)+C_2(I_2-3), \quad (7)$$

[3] L. R. G. Treloar, Trans. Faraday Soc. **39**, 241 (1943).

which was first suggested by Mooney (see footnote 2) as suitable for describing the elastic properties of rubber. It is noted that eq 7 involves two physical constants for the material, C_1 and C_2.

If eq 7 is introducted into eq 4, we obtain

$$\Theta = 2\psi r(C_1 + C_2)$$

and

$$Z = -2\psi^2 a^2 C_2 - \psi^2(a^2 - r^2)(C_1 - 2C_2). \qquad (8)$$

The equations for Θ and Z, when W takes the form of eq 6, can be obtained by putting $C_2 = 0$ in eq 8.

We see that if the physical properties of the material are represented by either eq 6 or 7, the force, Z, that must be exerted at each point is proportional to the square of the amount of torsion. If eq 6 applies, Z must everywhere have the nature of a thrust (as C_1 is essentially positive), which is distributed over the diameter of a plane and as shown in figure 1 (a). If eq 7 applies, then Z does not vanish at the periphery (where $r = a$), and provided C_2 is positive and sufficiently small compared with C_1, its distribution will have the form shown in figure 1 (b).

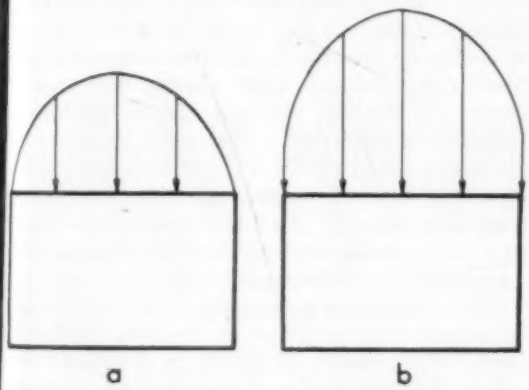

FIGURE 1.—*Distribution of normal surface traction over plane ends of cylinder in pure torsion.*

(a) when $W = C_1(I_1 - 3)$, and (b) when $W = C_1(I_1 - 3) + C_2(I_1 - 3)$.

IV. Experimental Procedure

The experiments which will be described in this paper have as their object the study of the distribution of the normal force, Z, defined in the previous section, and its dependence on the amount of torsion.

In a preliminary qualitative experiment a rubber cylinder of pure gum compound, with brass plates bonded onto its plane ends, was subjected to a torsional couple by means of a lever attached to one of the ends, while the other end was held in a vise. It was found that unless a longitudinal thrust was intentionally exerted parallel to the axis of the cylinder, the cylinder elongated, its axial cross section before and after torsion being shown roughly in figure 2. This simple experiment

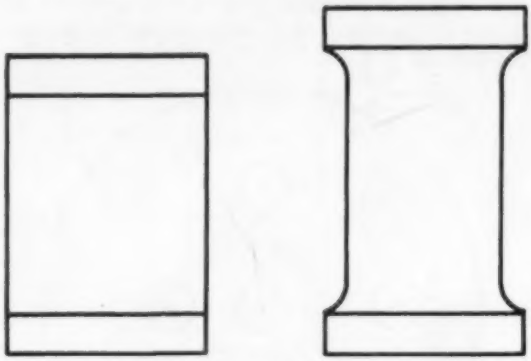

FIGURE 2.—*Axial cross section of cylinder before and after twisting by couple.*

bears out the mathematical conclusion that a pure torsional couple does not give rise to a pure torsion. Clearly, if a pure torsion is to be obtained, normal compressive forces, whose resultant must have the nature of a thrust, must be exerted over the plane ends of the cylinder. This is in general agreement with the theoretical predictions outlined in the previous section.

Consequently, an apparatus was designed in which the pure-gum cylinder, to whose plane ends brass disks are bonded, is restrained from elongating. So, when one disk is rotated with respect to the other by the application of a torsional couple, the longitudinal thrusts required for the production of a pure torsion in the rubber cylinder are automatically called into play. The upper brass disk, A, contains five circular holes, each ½-in. in diameter, varying in distance from the center and spaced as shown in figure 3, in order to have as little mutual interaction as possible. The lower disk, B, has rigidly attached to it a steel disk, C.

The assembly of rubber cylinder and disks A, B, and C is held in a robust steel frame, D, as shown in figure 4. The upper disk is rigidly attached to the frame and the lower disk is capable of being rotated in its own plane about its axis, by means of a crowbar which is introduced into one of

a series of holes in steel disk C. Provision is made for holding the cylinder in a state of torsion by means of steel pegs, which can be introduced into one of the holes, E, in the frame. A scale is also provided for measuring the angle through which the lower disk is rotated.

When this disk is rotated, the rubber bulges slightly in the holes in disk A, and the amount of this bulging is assumed to be proportional to the thrust which would have to be exerted to prevent the bulging.

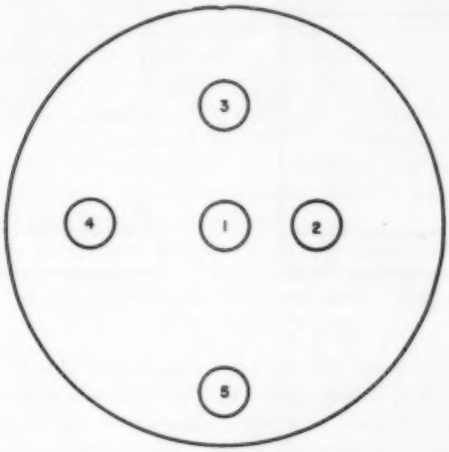

FIGURE 3.—*Upper brass disk.*

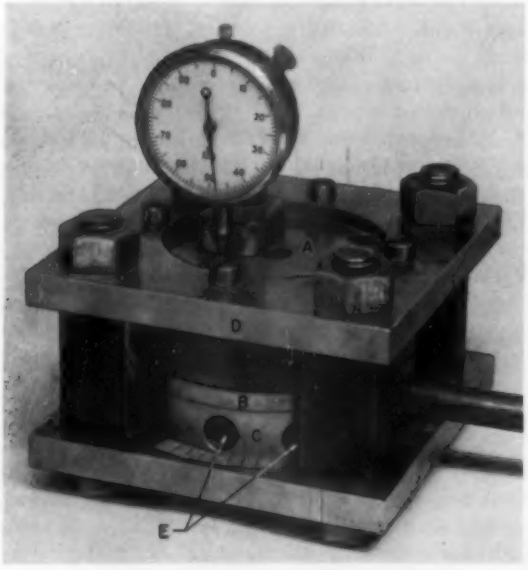

FIGURE 4.—*The torsion apparatus.*

The bulging represents a small deformation superposed on a relatively large torsional deformation. At each of the holes this torsional deformation approximates to a state of simple shear of an amount depending on the amount of the torsion and the position of the hole considered. The assumption that the amount of bulging is proportional to the normal force tending to produce it, is equivalent to an assumption that the former does not depend greatly on the state of simple shear on which the bulging deformation is superposed. There are certain theoretical reasons for assuming that this is approximately valid in the experiments described here.

In order to produce a simple extension in a cylinder superposed on the simple torsion, an additional normal surface traction must be exerted over each of the plane ends. If the stored-energy function of the material for the cylinder has the form of eq 6, it has been shown (see footnote 1) that this additional normal surface traction is independent of the amount of torsion and of position on the surface of the cylinder. The stress distribution in the neighborhood of the hole is complex, but for small deformations it is reasonable to assume that the amount of bulge in each hole is dependent only on the force tending to produce the bulging and not on the amount of torsion or position of the hole, except insofar as this force is determined by them. This conclusion should be approximately valid if the stored-energy function has the form of eq 7, provided C_2 is small compared with C_1. However, there is no reason to believe that it should be true for every possible form of the stored energy function.

The amount d of the bulging in each of the holes is measured at the center of the hole, for various angles of rotation, θ, of disk B, by means of a dial gage. The top of disk A is ground flat and used as a reference plane in carrying out this measurement.

V. Experimental Results

If eq 8 is valid for Z, then the relation between d and θ should be

$$d=K\theta^2[2a^2C_2+(a^2-r^2)(C_1-2C_2)], \qquad (9)$$

where K is some constant of proportionality, r is now taken as the distance of the center of the hole from the center of the disk. This assumption is justified if the radius of each hole is small compared

with that of the cylinder, but it is impracticable to make it too small as the values of d are thereby reduced. The repeatability with which d could be measured in the experiment was estimated as ± 0.002 in. using the same dial gage. The accuracy with which θ could be measured in the arrangement employed was $\pm \frac{1}{2}°$.

The gum compound used had the following composition in parts by weight:

Rubber	100
Sulfur	3.0
Captax	0.8
Stearic acid	1.0
Agerite	1.0
Zinc oxide	5.0
Tuads	0.08

The mix was vulcanized for 30 min at 134° C.

In order to produce a strong bond between the brass plates, a "tie gum" layer, less than $\frac{1}{32}$ in. thick, was introduced between the main rubber cylinder and each of the brass plates and a cement marketed as "Reanite, No. 3615" was employed. The composition of the "tie gum" layer was, in parts by weight,

Rubber	100
Stearic acid	1.0
Sulfur	3.5
Captax	1.0
Zinc oxide	5.0
Thermatomic black	40

The rubber cylinder employed had a radius of 2.12 in. and a length of 1 in. The holes in disk B each had a diameter of $\frac{1}{2}$ in., and the distances, r, of their centers from the center of the disk are:

Hole number	1	2	3	4	5
r, in in.	0	0.85	1.18	1.47	1.69

Equation 9 suggests that the results of the experiments be plotted as a relation between d and θ^2 on linear graph paper. This should yield a straight line passing through the origin for each hole.

This is done in figure 5 for each of the five holes, and it is seen that the linear relations between d and θ^2 of eq 9 are borne out within the accuracy of the experiment.

The slope, m, of the straight line obtained for each hole is the value of $K[2a^2C_2+(a^2-r^2)(C_1-2C_2)]$ for that hole, and if this is plotted

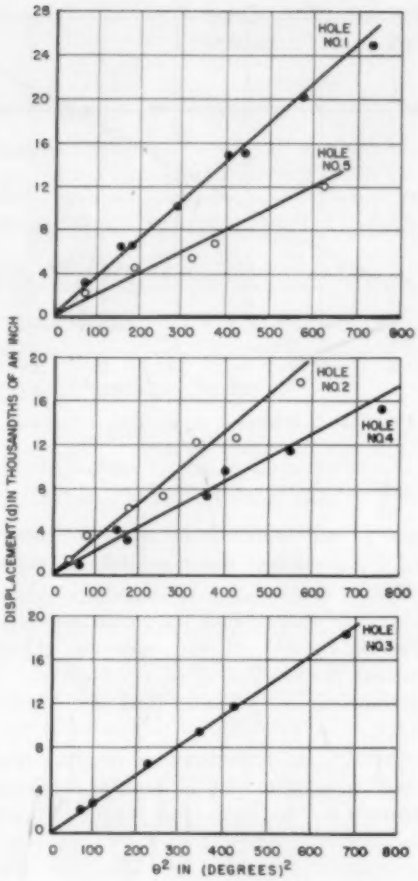

FIGURE 5.—*Relation between displacement and the square of the angle of torsion.*

against (a^2-r^2), a straight line should be obtained, which passes through the origin if $C_2=0$ and otherwise gives an intercept of $2a^2C_2K$ on the m-axis. If m is plotted against (a^2-r^2) as in figure 6, it is seen that, within the accuracy of the experiment, the relation eq 9 between d/θ^2 and (a^2-r^2) is again borne out.

If m_0 is the intercept of the straight line in figure 6 on the m-axis and b is its slope, we have $m_0=2a^2C_2K$ and $b=K(C_1-2C_2)$, whence

$$\frac{C_1}{C_2}=\frac{2b}{m_0}a^2+2 \tag{10}$$

From measurements on figure 6, we obtain $m_0=10\times10^{-6}$ in. deg.$^{-2}$, and $b=5.65\times10^{-6}$ in. $^{-1}$ deg.$^{-2}$, so that $C_1/C_2=7.1$.

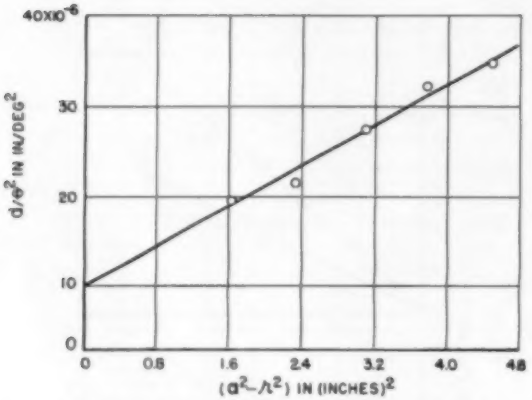

FIGURE 6.—*Relation between slopes of lines in figure 5 and positions of holes.*

The equation showing the relation $d/\theta^2 = K[2a^2C_2+(a^2-r^2)(C_1-2C_2)]$

Mooney (see footnote 2) uses the constants C_1 and C_2 to define three additional constants as follows: $G=2(C_1+C_2)$; $H=2(C_1-C_2)$; and $\alpha=H/G$. He then shows that constant G is the modulus of rigidity of the material. Constant α is named the coefficient of asymmetry. From the definitions it follows that $\alpha=(C_1/C_2-1)/(C_1/C_2+1)$.

Consequently, the experimental results presented here lead to a value of 0.75 for the coefficient of asymmetry of the pure-gum compound studied. This is somewhat larger than the values found for two compounds studied by Mooney. Further work would be required to establish the variation of α with the nature of the compound.

VI. Conclusions

The experiments bear out the general conclusion of the theory that in order to produce pure torsion in a rubber cylinder, normal surface tractions must be exerted on the plane ends and that these surface tractions vary with the amount of torsion and the position on the plane end of the cylinder. If the assumption is made that the amount of bulging in each hole is proportional to the for producing it and does not depend on the state local strain on which the bulging is superpose then the results of the experiments are in a cordance with the assumption of an expression the form of eq 7 for the stored-energy function the rubber. It has already been pointed out b Mooney that a stored-energy function of this for describes the linear shearing stress vs. amount shear relation for rubber in simple shear, with fair measure of accuracy, up to reasonably lar deformations. Also, Treloar [4] has recently o tained results in agreement with this for pur homogeneous strain of a sheet of rubber.

The form of eq 6 for the stored-energy functi is that derived from the kinetic theory of rubbe like elasticity. Load versus deformation relatio derived from this have been compared with e perimental results for simple types of deformati and have yielded fairly good agreement, depen ing on the type of deformation employed.

It appears then that eq 6 for the stored-ener function provides a first approximation to t stored-energy function for vulcanized rubber a that a second approximation is provided by eq The differences between these forms are more less accentuated depending on the type of d formation studied.

This work forms part of a program of fund mental research on rubber undertaken by th Board of the British Rubber Producers' Researc Association. The work was carried out at th National Bureau of Standards, Washington, D. C where the author is at present a guest worke The author is indebted to W. L. Holt of th National Bureau of Standards for advice an assistance in connection with the mechani design of the apparatus.

WASHINGTON, February 25, 1947.

[4] L. R. G. Treloar, Trans. Faraday Soc. (pending publication).

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Compensation of the Aperture Ratio Markings of a Photographic Lens for Absorption, Reflection, and Vignetting Losses

By Irvine C. Gardner

At present the diaphragm markings of a photographic lens are based entirely upon geometrical considerations and do not take into account the losses of light resulting from absorption, reflection, and scattering. A method of equivalent marking is described in which, for example, the marking 8 does not correspond to the geometrically determined aperture ratio 1:8 but to an opening sufficiently larger to permit the transmission of as much light as would be transmitted by the aperture 1:8 in the absence of any losses due to absorption, etc. Such a system of apertures may be referred to as equivalent, or compensated, apertures. Two systems of compensation are given, one based upon the illumination at the center of the field and the other based upon the average illumination over the entire field, thus taking vignetting into account.

A relatively simple photometric procedure for determining either of the two systems of compensated graduations is described. For use during a transition period, a system of markings is described that will permit exposures to be determined either with light losses compensated or by the present method without compensation. Except for the change of markings on a lens, no other instrumental changes are required to apply the new system of exposure determination.

I. Introduction

Photography is both an art and a technic. til a few years ago it was largely empirical, h photographer's practice being based on his experience with his own particular equipment. w, however, the principles underlying photo- phic work are so well known, and quantitative tions are so precisely established, that photo- phic engineering may be said to have become applied science. The possibility of saving e sums of money and at the same time secur- greater uniformity of result by greater preci- in the exposing and processing of the very e quantity of film used for motion picture photography has constituted an economic urge in favor of this transformation. The development of the modern photoelectric exposure meter and the more general dissemination of quantitative information regarding the properties of emulsions have made it possible not only for the professional, but also for the skilled amateur to control his photographic work in a scientific manner.

With this progress a demand has arisen for a more scientific method of marking the diaphragm openings of a lens. The method now in general use is based entirely upon the diameter of the entrance pupil and the equivalent focal length.

It gives no consideration to the loss of effective light that arises because of absorption in the glasses of which the lens elements are made or because of reflection and scattering at the surfaces. Photographic objectives in common use may have from 4 to 10 glass-air surfaces. The transmissions of such lenses may range from 50 to 80 percent if uncoated and may be as high as 95 percent if efficient low-reflection coatings are applied to the surfaces. It is evident, therefore, that the effective exposures for different lenses with the iris diaphragm set for the same aperture ratio, may vary almost by a factor of 2, an uncertainty that is inconsistent with the precision with which the other factors governing exposure are controlled. Several methods for calibrating and marking the apertures of a photographic lens that will effect a correction for the varying light losses with different lenses have been proposed.

This publication presents a method that is relatively simple and direct, and by which different laboratories may be expected to arrive at the same system of marking and equivalent values without the interchange of physical standards. The method is extended to apply to lenses when focused for infinity or for any finite distance, and a system for marking the diaphragm scale is suggested. In order to distinguish between the older and newer systems of marking, the aperture ratio of the older system, based on geometrical measurements only, will be referred to as the *geometrical aperture ratio*. The new aperture ratio, which takes the absorption and reflection losses into consideration will, for present purposes, be designated the *equivalent aperture ratio*. Other terms that might be used are *compensated aperture ratio*, and *t-aperture ratio*, the t standing for transmission as suggested by Berlant.[1] Consideration is also given to the difference in performance of different lenses because of vignetting.

II. Method of Calibration for Infinite Object Distance

In figure 1, L represents a photographic lens that receives light from the uniformly illuminated screen CD. In the focal plane there is the plate GH, with the aperture of area A centered at O. Behind this aperture there is a photoelectric cell with receiver R, which is large enough to receive all the luminous flux from screen CD that is transmitted by the photographic lens and the aperture at O. The full lines represent the boundary of the cone of rays proceeding from the screen to the axial point of the focal plane. In the object space the cone degenerates into a cylinder, of which the diameter is d. In the image space the half-angle of the cone is α, where α is defined by the equation [2]

$$\sin \alpha = d/2f. \tag{1}$$

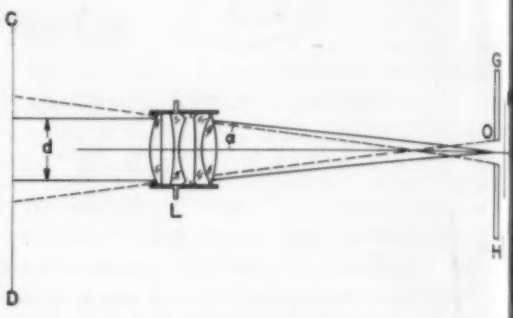

FIGURE 1.—*Arrangement of apparatus for measurement of total luminous flux transmitted through a photographic objective and through an aperture of area A in the focal plane at O.*

The geometrical aperture ratio is 1:1/(2 sin α).

The aperture ratio of the lens, for an infinitely distant object, is 1: f/d, and f/d is the f-number. It is evident that

$$f\text{-number} = \frac{1}{2 \sin \alpha}$$

In figure 2, CD represents a uniformly illuminated screen identical with that of figure 1. Screen GH with aperture, of area A at O, and photoelectric cell with receiver R are identical with the similar parts of figure 1. At IJ, at a distance e from the plane GH, there is a circular diaphragm of diameter such that the angle, α, in figure 2 equals the corresponding angle of figure 1. For the moment it will be assumed that the length e, is identical with the equivalent focal length of the photographic objective of figure 1. If B is

[1] E. Berlant, Lens stop calibration by transmission, J. Soc. Motion Picture Engrs. **46,** 17 (1946); C. R. Daily, A lens calibrating system, J. Soc. Motion Picture Engrs. **46,** 343 (1946); A. E. Murray, The photometric calibration of lens apertures, J. Soc. Motion Picture Engrs. **46,** 142 (1946).

[2] There is a temptation to write this equation tan $\alpha = d/2f$, but if the lens is suitably corrected for coma, a necessary condition for a photographic objective, eq 1 is correct.

brightness[3] of the screen CD, and if one assumes a very small area, ΔA, at O, normal to the axis of the lens and including the axial point, the total luminous flux ΔF received by this area is given by the equation

$$\Delta F = B\Delta A \sin^2 \alpha, \tag{3}$$

this being exact in the limit as ΔA approaches zero. If it is assumed that the actual area at O,

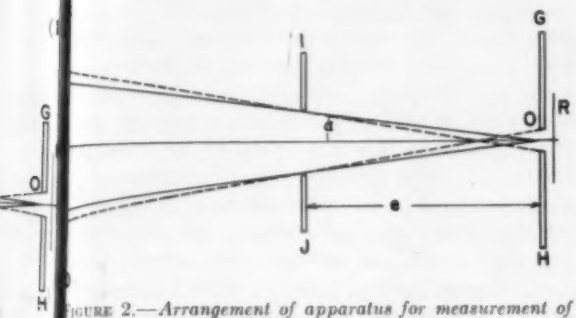

FIGURE 2.—*Arrangement of apparatus for measurement of total luminous flux transmitted through aperture IJ and through the aperture of area A at O.*

This flux equivalent to that transmitted by a lens free from absorption and reflection losses and with the aperture ratio $1:1/(2\sin\alpha)$.

for which the incident luminous flux is measured has a maximum radius, r, such that the ratio r/e does not exceed 0.02, for most photographic purposes, the equation

$$F = BA \sin^2 \alpha \tag{4}$$

is sufficiently exact, where F is the total luminous flux incident upon the area A in the focal plane. For the arrangement of figure 2 the *geometrical aperture ratio* and the *equivalent aperture ratio* are identical, because for the opening, IJ, there are no reflection or absorption losses.

[3] Throughout this discussion the terms *illumination* and *brightness* are employed. These terms usually refer to measures of radiant energy evaluated in terms of the luminosity curve and apply strictly only when the energy receptor is the eye or a detector having the same sensitivity curve. Strictly speaking, when discussing photographic applications, terms referring to radiant energy evaluated in terms of the wavelength sensitivity of the photographic emulsion should be used. This paper is concerned chiefly with ratios of two similar measurements of radiant energy and, inasmuch as optical glass, the only absorbing material concerned shows little selectivity over the range of wavelengths under consideration, all equations are true, to a satisfactory approximation, whether they are considered to apply to light (in the restricted sense) or to radiant energy affected by the photographic sensitivity curve. The justification for the use of the terms applying to light is greater because there has been no general agreement on terms to be applied to radiant energy evaluated in terms of photographic sensitivity.

Referring now to figure 1, the total luminous flux, F, falling upon the area A will be given with sufficient exactness by the equation

$$F' = BAk \sin^2\alpha, \tag{5}$$

k being the transmittance of the lens.

The values of F and F' will be indicated by the photocell, if it is suitably calibrated. It is at once apparent that if B, A, and α are held constant for the two measurements, the transmittance is given by the equation.

$$k = \frac{F'}{F}. \tag{6}$$

On the other hand, suppose that the iris of the photographic lens or the diaphragm, IJ, of figure 2 is adjusted until $F = F'$. Let α_1 be the value of the half-angle of the cone in figure 2 for which this equality is obtained. The aperture ratio corresponding to α_1 is $1:(1/(2\sin\alpha_1))$ and the f-number is $1/(2\sin\alpha_1)$. For this adjustment, it follows that the light transmitted by the photographic lens is equal to that which would be transmitted by a lens of zero absorption and with the aperture ratio $1:(1/(2\sin\alpha_1))$. This method, therefore, provides a means for calibrating a lens in such a manner that the absorption losses are compensated.

Table 1 gives the values of α corresponding to values of the aperture ratio that are commonly represented on photographic shutters.

TABLE 1.—*Half-angles, α, corresponding to standard aperture ratios*

Aperture ratio	α	Aperture ratio	α
	Degrees		*Degrees*
$1:1.4_1$	20.77	$1:11.3_1$	2.53
$1:2.0_0$	14.48	$1:16.0_0$	1.79
$1:2.8_2$	10.18	$1:22.6_2$	1.27
$1:4.0_0$	7.18	$1:32.0_0$	0.896
$1:5.6_4$	5.07	$1:45.2_5$	.633
$1:8.0_0$	3.58	$1:64.0_0$	.447

To calibrate a lens, therefore, it is only necessary to have a series of diaphragms that, for the length e, will correspond to the different required values of α. A photocell reading is taken with the arrangement of figure 2, after which the photographic lens is substituted for the diaphragm and the iris adjusted until the same reading is obtained. This setting corresponds to the given geometrical aperture ratio and zero absorption. If, on the other hand, it is desired to determine the equiva-

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lent aperture ratio corresponding to the maximum indicated geometrical aperture ratio, it is necessary to secure the balance between measurements of figures 1 and 2 by adjusting the diameter of aperture *IJ* in figure 2.

Some of the details and necessary precautions can now be profitably considered. It is not necessary that length ϵ of figure 2 be exactly equal to the focal length of the lens being tested, provided that the correct ratio is maintained between ϵ and the diameter of the aperture. It is desirable that ϵ be approximately equal (within 5% is satisfactory) in order that the approximation introduced by the finite area *A* shall not differ greatly for the two measurements. Area *A* must be definitely limited and, when the lens is used, it should be located accurately in the focal plane. A suitable way to achieve this is by the use of a metal plate in the focal plane with a circular aperture of the desired area and a photocell back of the aperture with a receiver large enough to receive all the light that passes through the opening. Such a plate is indicated at *GH* in figures 1 and 2. The dotted lines in figure 1 and 2 indicate the portion of the screen *CD* that contributes to the illumination at *O*. It is evident that the contributing areas for the lens and for the aperture will be smaller and more nearly identical if the screen *CD* be brought close to the lens or diaphragm respectively.

It is therefore recommended that screen *CD* be placed immediately in front of the lens and illuminated by transmitted light. Uniform brightness of the smaller area thus utilized is more easily obtained, and deficiencies in uniformity of illumination become less important as the areas utilized during the two measurements become more nearly identical. It is, of course, essential that the brightness of the screen have the same value for the measurement with the diaphragm and with the lens. It is also assumed that all parts of screen *CD* contributing to either measurement obey Lambert's law. In other words, a collimated beam or a surface giving specular reflection should not be used.

There are variations of the experiment that suggest themselves. For the evenly illuminated screen *CD*, an integrating sphere may be substituted. Furthermore, the directions of the light may be reversed with the source at *O* and the receiver at *CD*. In this latter case, if *CD* is not replaced by an integrating sphere, the receiver o the light-sensitive element must be large enough to receive all the luminous flux, and it must be uniformly sensitive over the entire area. This requirement can be most easily met if the receive is placed near lens *L* or aperture *IJ*, as the required size is then greatly reduced.

Strictly speaking, the spectral quality of the ligh proceeding from source *CD* when the measurement are made should be identical with that reflected from the object to be photographed, and the spectral sensitivity of the photocell should be identical with that of the emulsion to be used. When the great variations usually present in the spectral quality of the light proceeding to a lens from a object to be photographed are considered, it is evident that it is not practicable to fulfill this condition. Fortunately, the absorption of a photographic lens is not particularly selective for different parts of the spectrum, and the values of *k* for a given lens will not differ greatly as the spectral distribution of the light illuminating screen *CD* is changed. However, for precise work, standardization is desirable, and it is accordingly suggested that tungsten lamps operating at a color temperature of 2,360° K be used in conjunction with Wratten No. 79 filters. This gives light having a color temperature approximately that of the noon sun (5,400° K). The use of a controlled source facilitates intercomparison between measurements at different laboratories. Even in the absence of such a standardized source, if screen *CD* is illuminated by tungsten lamps operating at normal voltage, and if the photocell has a spectral sensitivity similar to that of the commercial exposure meter, the use of the equivalent aperture ratios, measured by the method of this presentation, will be much more precise and accurate than the use of the geometrical aperture ratios.

III. Method of Indicating Equivalent Aperture Ratios

According to the current method of determining aperture ratio, the diaphragm markings on the lenses will not yield consistent exposures from lens to lens. Either the speed ratings of the emulsions or the computing tables on the exposure meters, or both, may be considered as adjusted to give the correct exposure for some average value of

k_0, typical of photographic objectives. For a lens having a value of k_0 smaller than this average value, the result will be underexposure, and for a lens having a higher value (for example, a coated lens), the result will be overexposure. If this assumed value of k_0 were known, it would be possible to alter the speed rating of the emulsions to give correct exposure with lenses graduated to read equivalent aperture ratios. To illustrate, if it were known that the value of k_0 is 0.76, for the average lens[4] is the basis on which the computation tables of a certain make of exposure meter rests, the speed rating of a photographic emulsion for use with the equivalent aperture ratios should be increased by the factor 1/0.76. Once this adjustment of speed ratings has been made, exposures should be selfconsistent for all lenses graduated in terms of the equivalent aperture ratio.

Figure 3 A shows the diaphragm markings of a lens developed into a linear scale. Between each pair of graduations there is a dot. The indicated graduations with numbers correspond to the geometrical aperture ratios as now marked on photographic lenses. The dots correspond to the equivalent aperture ratios, each dot representing the equivalent aperture ratio of the same value as the next smaller geometric aperture ratio. To illustrate, the dot between 2.8 and 4 corresponds to the equivalent aperture ratio 1:4, and similarly, the dot between 5.6 and 8 corresponds to the equivalent ratio 1:8. Such dots in red have been used at times on photographic lenses.[5]

This method of marking may not be entirely unambiguous, as there is a possibility of allocating the dot to the incorrect one of the two adjacent stop numbers. Consequently, the marking shown in figure 3B is suggested. In this case a line, preferably red, is drawn connecting the setting for the equivalent aperture ratio to the corresponding geometrical aperture ratio graduation. The length of this line indicates the extent to which a lens aperture must be opened beyond a given *geometric aperture ratio* to compensate for the loss of light resulting from reflection and absorption. Having a lens doubly marked in this manner is certainly an advantage during a period of transition when one is changing from the regular use of one set of markings to the other. In addition to marking the lenses, the only change required is the publication of a new set of speed ratings. During the transition period the manufacturers might well give two sets of speed ratings in their tables, one in black for use with the geometrical aperture ratios, and one in red for use with the equivalent aperture ratios. Even after the use of the equivalent aperture ratios has become general, it might well be desirable to retain the double system of marking on photographic lenses because the geometrical aperture ratios apply more precisely to the depth of focus scales with which many cameras are now provided.

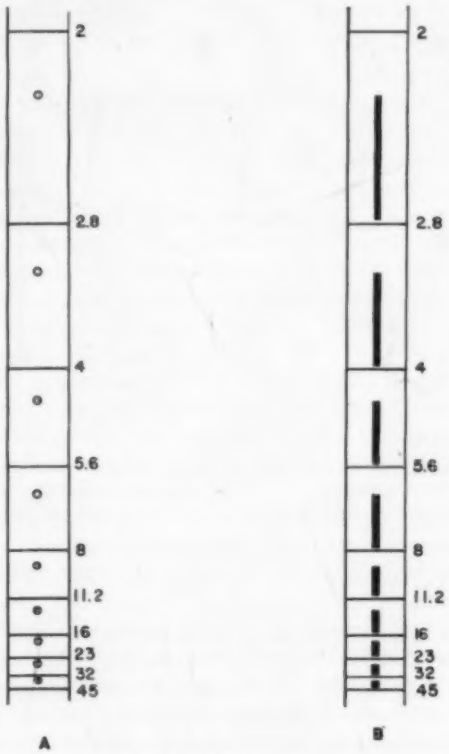

FIGURE 3.—*Methods of indicating the effects of aperture ratios.*

A, Aperture scale of a typical lens with the geometric aperture ratios indicated by the graduations and numbers in the conventional manner. Dots (which preferably are in red) indicate the settings for the equivalent aperture ratios. To illustrate, the dot between the graduations 5.6 and 8 corresponds to the equivalent aperture 1:8; B, preferred system of marking the equivalent aperture ratios in which a line (preferably red) connects the setting for a given equivalent aperture ratio with the geometrical aperture ratio having the same numerical value.

[4] W. N. Goodwin, Jr., J. Soc. Motion Picture Engrs. **20**, 95 (1933).

[5] Paul C. Foote, of Bell & Howell Co. has mentioned this type of marking and has made photographs available of a graduated Leica lens.

IV. Effect of Vignetting

The measurements of section II have been concerned only with the illumination on the axis of the lens. In figure 2, if the aperture O and receiver R are displaced the distance $\epsilon \tan \beta$ in a direction normal to the axis of the diaphragm, as shown in figure 4, a measure of the flux corresponding to an image point at an angular displacement, β, from the axis is obtained. This will be less than the axial value because of the operation of the "cosine fourth-power law," which is a statement that the illumination in the field of a photographic lens varies as the fourth power of the cosine of the angular distance from the center of the field provided that the diameters of all elements of the lens system are so great that the iris of the lens is the only part of the system that restricts the cone of transmitted rays. Although this last restriction is seldom fulfilled over the entire field of a lens, it should be noted that even when this condition is complied with, the cosine fourth-power law is an approximate rather than an exact statement.

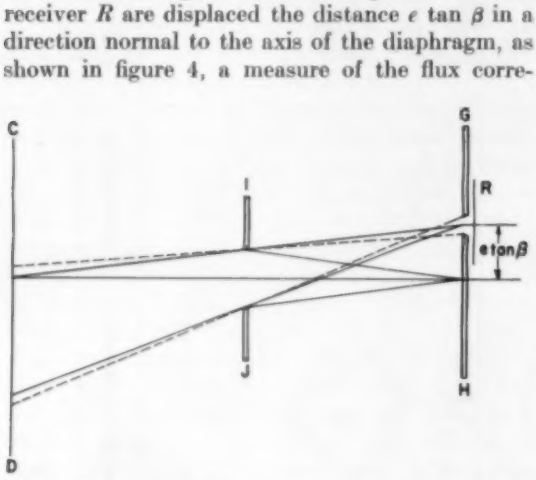

FIGURE 4.—*Arrangement of apparatus for measuring the total flux transmitted through aperture IJ and through the aperture of area A displaced from the axial position.*

The measurements made with arrangements indicated in figures 2 and 4 give a measurement of the decrease of illumination for points off the axis when there is no vignetting.

The ratio of the illumination at the off-axis position to the axial value gives a measure of the decrease of illumination as the image point moves from the center of the field outward. Let F_β and F_0 be the fluxes measured by the apparatus, as shown in figures 2 and 5 respectively. Then the ratio F_β/F_0 gives the ratio of the exposures β degrees from the axis and on the axis for an ideal lens with no absorption and no vignetting.[6]

The ratio F_β/F_0 will approximately equal $\cos^4\beta$.[7]

Similarly, for the arrangement of figure 1 aperture O and receiver R may be displaced through the distance $f \tan \beta$ and a measurement of the illumination made. It will be assumed that the iris is set for an equivalent aperture ratio the same as that for the measurements of figures 2 and 4. We now have four readings, F_0', the axial value for the arrangement of figure 1; F_β', the reading for the arrangment of figure 1 with the measurement made β degrees from the axis; and F_0 and F_β. Since the equivalent aperture ratios are assumed to be the same in all cases, $F_0'=F_0$. The ratio F_β'/F_β gives a measure of the vignetting, i. e., the falling off in illumination beyond that attributable to an ideal lens.[6] However, the ratio F_β'/F_0' is the more useful ratio to the lens user because it gives directly the ratio of the exposure obtained at a point β degrees from the axis to that obtained on the axis.

Different types of lenses differ greatly in the amount of vignetting. A lens system that is long in comparison with its focal length requires much larger elements than a short lens system if vignetting is to be avoided or reduced to a satisfactory value. Sometimes a lens system is such that the aberrations for the marginal parts of the field are excessive. Such a fault is rendered less apparent when there is considerable vignetting because the lens is, in effect, stopped down at the edge of the field much more than at the center. Excessive vignetting is sometimes found in folding hand cameras because the manufacturer, in order to make the camera compact, makes the lens elements small. If, for example, the lens is rated as an $f/2$, this relative aperture may apply only at the center of the field, the exposure falling off very sharply for the corners of the picture.

[6] "Vignetting" is ambiguous unless defined. It may reasonably be applied to include all the decrease of illumination that arises at an off-axis point in the image-plane of a photographic objective, or the term may be used to apply only to the decrease of illumination which arises because of restrictive action of parts of the lens mount or lens elements and which is in excess of that necessarily occurring with an ideal lens. Following the custom of several writers, the second application is used in this discussion. In accordance with this interpretation, there is no vignetting for the system of figure 4.

[7] This is not strictly true, because the illumination resulting from the aperture of fig. 2 does not fall off exactly as the fourth power of the cosine. The diaphragm, however, represents a convenient standard that can be reproduced without difficulty at different laboratories and it follows the cosine fourth-power law as closely as do most lenses in common use. The approximation is better for the smaller apertures and for points near the axis. To illustrate, for points distant 40 degree from the axis, the departures are 7.6, 1.8, and 0.4 percent for the aperture ratios 1:2, 1:4, and 1:8 respectively.

For such a lens, the vignetting rapidly becomes less as the lens is stopped down, and such an arrangement does not necessarily represent an undesirable compromise. The user has a compact camera without excessive vignetting for the aperture ratios that are usually used with modern rapid film and at the same time has high speed, at least for the central part of the picture, for the occasions when it is required. However, when exposures are made on color film with the maximum aperture, such vignetting, because of the generally reduced latitude of color film, may be sufficient to detract from the effectiveness of the picture

V. System of Stop Calibration that Gives Weight to Vignetting

The method of stop calibration of section II compensates for the different transmittances of different photographic objectives and insures equivalent exposures at the center of the image field for different lenses when used at the same equivalent aperture ratios. However, it does not distinguish between the behaviors of different lenses that arise because of the differences in vignetting. In figure 5 the arrangement is the same as for figure 1, except that instead of measuring the illumination of a small area near the axis, the total flux received by an area in the focal plane identical with the picture frame is measured. Similarly, for the comparative measurement with an aperture only, the arrangement of figure 2 is modified to give a measurement of the flux received by the entire field. The equivalent aperture ratios, as before, are considered equal when the two flux measurements are equal. If e of figure 2 and f of figure 6 are not equal, the angular subtenses of the two field-stops at the center of the diaphragm and exit pupil of lenses must be equal when the two measurements of flux are made, and the differences in area should be considered. For photographic purposes, the agreement will be satisfactory, provided that the two field apertures are identical and the value of e and f do not differ by more than 1 percent.

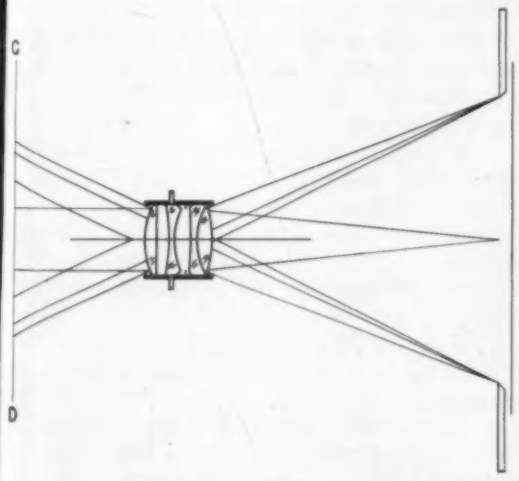

FIGURE 5.—*The aperture in plate GH includes the entire field of view utilized when the lens is mounted for use in a camera.*

The measurement of luminous flux obtained under this condition is characteristic of the average illumination over the entire field instead of the illumination at the center of the field as obtained by the arrangement of figure 1.

For a motion-picture camera or a miniature camera, the field aperture required is small, and it is generally not too difficult to make the measure as outlined. If the picture frame is large, it may be desirable to reverse the direction of travel of the light by using an integrating sphere to illuminate the picture frame. The total flux is then measured by a photoelectric element with a receiver large enough to receive all the light that passes through the lens. By this reversal of the direction of travel of the light, a photocell with a receiver smaller than otherwise applicable can be used.

If the iris of a lens is calibrated by the two methods, measuring central illumination only and measuring the flux received by the entire field, it will be found that the calibrations, in general, are different. This is understandable because the two methods are based upon different assumptions. In the method first described, a given equivalent aperture ratio corresponds to a definite illumination at the center of the image field. According to the second method, the use of the equivalent aperture ratio corresponds to a given average illumination over the entire field. For a lens that has a large amount of vignetting, a given geometric aperture ratio will correspond to a smaller equivalent aperture ratio than for a lens with less vignetting. Both methods of calibration have advantages, and it is probable that the different standardizing groups interested in photographic procedure should carefully consider the two methods and make recommendations governing their use.

VI. Calibrations of Stop for Finite Object Distances

In the foregoing discussion, it has been tacitly assumed that the object to be photographed is at an "infinite" distance and that the image will consequently lie in the focal plane of the lens. This is the basis on which the values of the geometric aperture ratio are engraved on the lens mounts, and it is an entirely satisfactory procedure for a large amount of photographic work. If, for example, the object instead of being at an "infinite" distance is only 10 focal lengths away, the distance from lens to focal plane is only increased by 10 percent of the equivalent focal length and, for many applications, the error in exposure resulting from using the values corresponding to the image in the focal plane will not be excessive.

Lenses for copying purposes and some other types are habitually used with the object distant only a few focal lengths from the lens. In such instances it is highly desirable that the aperture ratios be marked for one or more selected object distances approximating those which will actually be employed in practice. The method of stop calibration can be readily extended to apply to this problem.

Suppose, for example, that the selected object distance is $2f$, corresponding to the use of the lens for one-to-one copying. Referring to figure 1, plate *GH* bearing aperture *O* will be moved back from the lens to the image plane corresponding to one-to-one copying. Referring to figure 2, plane *GH* will be separated from the diaphragm by approximately the same distance as for the lens. For this particular case, the separation would be twice the equivalent focal length of the lens. With this new spacing, the diameter of aperture *IJ* should be determined, so that sin α has a value corresponding to a selected aperture ratio, as given in table 1. Measurements are now made as before, the diaphragm setting of the lens being altered until the two flux readings are the same. When equality is obtained, the equivalent aperture ratio of the lens, for the one-to-one ratio, is equal to the geometrical aperture ratio of the diaphragm.

If the iris markings are calibrated in this manner, the lens will give the same exposure for a given equivalent aperture ratio and one-to-one copying as does the same lens or any other lens with the calibration for infinite distances when used on a distant object. For a finite distance, the question again arises as to whether the calibration should be similar to that of section II, with exposure at the center of the field as the criterion, or to the method of section IV, in which the criterion is average exposure over the entire field.

VII. Advantages of Proposed Method of Lens Aperture Calibration and System of Lens Marking

The foregoing text refers to several published papers dealing with this subject. The method of calibration and marking herein proposed offers advantages not possessed by any of the previously suggested methods:

1. The standard aperture to which reference is made is an aperture of known diameter in a metal plate, and therefore can be readily produced by any laboratory. This facilitates the maintenance of consistent systems of graduation by different laboratories.

2. Each calibration is essentially a substitution method in which the two values of flux to be measured are of approximately the same value. This largely eliminates errors arising from the nonlinearity of response of the photometric apparatus and eliminates the need for carefully calibrated filters.

3. No condenser or collimator system is used. Hence the method does not involve the assumption that the distribution of energy in a collimated beam is uniform.

4. A method of application is proposed that requires no modification of present models of exposure meters. New film-speed tables are required, but presumably the data already in the possession of manufacturers of exposure meters will be sufficient for the preparation of these tables.

5. A system of lens marking is proposed that permits exposure to be determined either by the conventional or new method.

6. An extension of the method of calibration has been given that permits lenses to be calibrated for object distances other than infinite.

7. The calibrated value may be based on brightness of image at the center of the field or on average brightness of image over all the field, whichever may be considered preferable.

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Heat Capacities of Gaseous Oxygen, Isobutane, and 1-Butene from −30° to +90° C

By Paul F. Wacker, Ruth K. Cheney, and Russell B. Scott

An adiabatic constant-flow calorimeter previously used was modified to improve its accuracy. The heat capacity of gaseous oxygen was measured at −30°, +40°, and +90° C, and the results were compared with values calculated from spectroscopic data. The experimental and spectroscopic values agreed within 0.04, 0.02, and 0.11 percent at the three temperatures. The heat capacity of isobutane was measured at −30°, +0°, +40°, and +80° C. A few measurements were made on 1-butene at 40° and 90° C. Measurements on the hydrocarbons at two or more pressures permitted the calculation of values of $(\partial^2 V/\partial T^2)_P$.

I. Introduction

In an earlier investigation [1][1] an apparatus was described with which the specific heats of several hydrocarbons were measured with an accuracy of about one-half percent. Since this first paper, a study of the possible sources of error suggested some changes in the apparatus. These changes resulted in a significant improvement in accuracy. The apparatus was tested by making measurements on oxygen, whose specific heat is accurately known from spectroscopic data. The results of the test showed that errors in the present experimental results are probably less than one-tenth percent.

The testing of an apparatus for the determination of heat capacities of gases with a material whose heat capacity is well known is strongly recommended as the consistent error in this type of apparatus may be large compared with the random error.

The measurements of the heat capacities of isobutane and 1-butene provide data that are valuable in combination with spectroscopic data for the calculation of thermodynamic functions over a wide range of temperature. Such measurements are most useful when they cover a considerable temperature range with high accuracy.

[1] Figures in brackets indicate the literature references at the end of this paper.

II. Materials

The impurities in the materials used in this investigation are believed to be of such nature and amounts as to have a negligible effect upon the specific heats.

The oxygen was prepared from water in a filter-press-type electrolytic generator used for the production of pure hydrogen in the Bureau's Cryogenic Laboratory. It was freed of hydrogen by passing the gas over hot palladium-coated asbestos. Then the oxygen was condensed and reevaporated four times to remove water. The product is believed to be of especially high purity.

The isobutane, designated as Research Grade Lot No. 5, was obtained from the Phillips Petroleum Co. A determination of freezing-point lowering by the Thermochemistry and Hydrocarbons Section of the National Bureau of Standards showed that a sample from this lot contained 0.12 ± 0.06 mole percent impurity. The sample in this investigation was found, by the Mass Spectrometry Section, to contain 0.04 mole percent diethyl ether and no more than 0.1 mole percent *n*-butane. No other impurity was found.

The 1-butene was supplied by the Phillips Petroleum Co. A measurement of freezing-point lowering made by J. G. Aston of Pennsylvania State College showed that a sample from the same batch had a liquid-soluble solid-insoluble impurity

of 0.46 percent. The Mass Spectrometry Section of the Bureau found the sample to contain 0.1 mole percent *n*-butane. They found no other impurity and were unable to detect any other butenes. However, the mass spectrometer would probably fail to detect less than 1 percent of other butenes.

III. Apparatus and Procedure

The flow calorimeter is shown in vertical section in figure 1. This is the apparatus described by Scott and Mellors [1], except for the following changes suggested by some calculations of the heat transfer in the calorimeter by Harold W. Woolley: (1) The portion of the calorimeter tube between the cold compartment and the heater was lengthened from 41 to 56 mm in order to reduce heat conduction along the tube. The thimble, *Th*, was correspondingly lengthened from 21 to 36 mm. (2) To avoid thermal contact between the calorimeter tube and the shield, *S*, the cord between the bottom of the shield and the tube was removed. The shield was then centered and supported from the outside by means of cotton-cord spacers held in place by a brass washer.

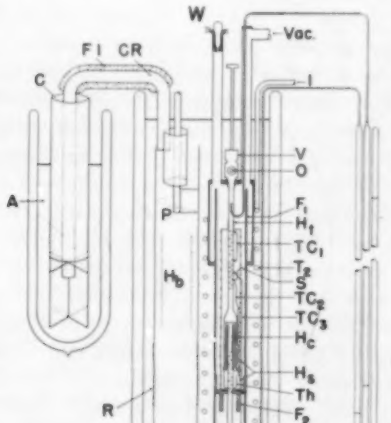

FIGURE 1.—*Scale diagram of calorimeter*

A, Liquid air; *C*, protecting cylinder; *FI*, felt insulation; *CR*, copper rod; *P*, propeller; H_b, H_1, H_c, and H_s, electric heaters; *R*, copper resistance thermometer; T_1, stirrer tube; *W*, wax seal; Vac, vacuum line; *I*, inlet; *V*, throttle valve; *O*, outlet; F_1, flange; TC_1, TC_2, and TC_3, thermocouples; T_2, helical tube; *S*, radiation shield; *Th*, metal thimble; F_2, flange; *B*, constant temperature bath; *M*, manometer.

The measurements of specific heats consisted of determinations of the rate of flow of the gas through the calorimeter, the electric power to the calorimeter heater, and the rise in temperature of the gas. Because of the pressure drop through the calorimeter and the resultant Joule-Thomson cooling, it was necessary to make auxiliary measurements of the decrease in the temperature of the gas flowing through the calorimeter when no power was supplied to the calorimeter heater.

The method of making the measurements was essentially the same as that previously described [1], although some improvements have been added. The following description is a brief review of the procedure, giving details only of the changes.

The gas entering the calorimeter was kept at nearly constant pressure by controlling the electric power supplied to an external boiler into which the material in the liquid state was introduced. The flow rate was fixed by setting the throttle valve, *V*, (fig. 1) at the beginning of an experiment. So that the flow rate might be as constant as possible, vapors on the low pressure side were condensed with liquid air. This was very satisfactory for condensing the hydrocarbons, but when oxygen was used the exhaust pressure was about 0.5 atmosphere. With oxygen, therefore, measurements of the specific heat at pressures below 1 atmosphere would not have been expected to be very accurate and were not carried out.

The rate of flow of the gas through the calorimeter was determined by condensing and weighing the gas that passed through in a measured time interval. Because the oxygen also was handled in this way, it was necessary to provide a weighing container of about 1 liter capacity that would safely hold a pressure of 100 atmospheres. Before starting to collect a sample to be weighed, a steady state was established with gas flowing to the waste container, and with the calorimeter heater turned on. Then the stream was diverted to the weighing container for a measured interval of time. In order to effect this change-over quickly and to measure the time interval accurately, the valve shown in section in figure 2 was designed. The gas from the calorimeter enters at *I* and can pass either to the waste container through C_1 or to the weighing container through C_2, depending on the position of the double-ended valve needle, *N*. The needle is moved by the lever, *L*, which is operated through the strip of spring steel by the

handle, H. The metal bellows, B, provides a gas-tight seal, yet allows the lever to pivot about the pin, P. Sw is an electric switch that remains closed while the gas is flowing into the weighing container. This switch engages the clutch of a synchronous-interval timer. The motor of the interval timer is driven continuously by a standard 60-cycle signal furnished by the Central Radio Propagation Laboratory of the National Bureau of Standards. The time can be read to 0.01 second, and it is believed that the time of operating the

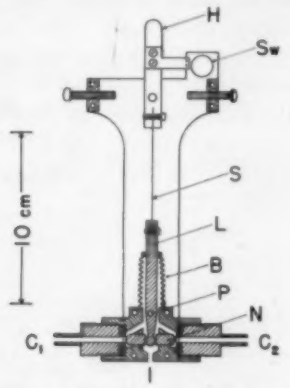

FIGURE 2.—*Scale diagram of two-way valve.*

H, Handle; *Sw*, electric switch; *L*, lever; *B*, metal bellows; *P*, pin; *N* needle; C_1, exit to waste container; *I*, gas inlet; C_2, exit to weighing container; *S*, strip of spring steel.

valve is less than 0.1 second. The difference between the time taken to open and close the valve could not have caused a significant error in the heat capacity, as the minimum time for a determination was 600 seconds.

The data on 1-butene were taken before the installation of this valve and switch but, for these measurements, the runs were of sufficient duration so that errors in starting and stopping were not important. The principal advantage of this valve lies in the fact that the flow, and therefore the equilibrium temperatures, are relatively undisturbed when the flow is diverted from one collecting reservoir to the other.

The power input to the calorimeter was determined with a Wenner potentiometer by measuring the current flowing through the heater and the potential drop across it. The temperature rise of the gas was measured by means of a five-junction copper-constantan difference thermocouple, TC_3. The wires of this couple make three turns around both the radiation shield and the flange, F_2, and are cemented with Glyptal lacquer. This brought the leads to the approximate temperatures of the junctions and so prevented significant differences between the temperatures of the thermocouple junctions and the adjacent parts of the calorimeter tube. The fact that the thermocouple was not calibrated in place is not believed to have caused an appreciable error as no significant differences in potential were found when the thermocouple was immersed varying amounts in the calibration bath, and as strains were avoided in those parts of the thermocouple in which there were temperature gradients Further, the calibration of the thermocouple is not believed to have changed with time, as no significant differences in potential were observed between points taken 2 months apart in the calibration of the thermocouple used in the present investigation. It is believed that the temperature intervals in the heat capacity measurements were determined to about one part in 5,000.

Small variations in the temperature rise of the gas, Δt, perhaps caused by small changes in the power input to the calorimeter heater, H_c, were compensated for by small adjustments of the input pressure. In this way, the temperature rise of about 10 degrees was maintained constant to about 0.01 degree. Furthermore, when a run was terminated, Δt was very constant and had the same value (within 0.001°) that it had at the start of the run. Thus the heat capacity of the calorimeter did not enter into the computations.

The Joule-Thomson correction for all three gases was determined by measuring the temperature decrease when gas was passed through the calorimeter without applying heat to the calorimeter tube, but with all other conditions the same as in a specific-heat run. These measurements were made at temperatures equal to the mean temperatures of the specific-heat runs and at various pressure drops and mean pressures. These measurements may include effects other than the Joule-Thomson effect and are more accurately called blank runs. The probable error in the heat capacity caused by the uncertainty in the blank runs is estimated as 0.03 percent.

IV. Test of the Apparatus with Oxygen

The heat capacity of oxygen was measured to test the accuracy obtainable with the calorimeter

after making the changes described in section III. Oxygen was used for this purpose because the specific heat is accurately known from spectroscopic data, and it could be condensed and weighed.

1. Observed Data

The observed heat capacity, C_P, in calories per mole-degree, was calculated from the relation

$$C_P = \frac{WM}{4.1833r(\Delta t + \delta t)}, \qquad (1)$$

where W is the heat input in watts, r is the flow rate in grams per second, M is the molecular weight, Δt is the temperature rise, and δt is the Joule-Thomson cooling in degrees centigrade. Equation 1 actually gives values of $\Delta H/\Delta T$, but for the temperature intervals chosen for these experiments $\Delta H/\Delta T = dH/dT = C_P$ within the precision of the data.

The determinations of the heat capacity of oxygen consist of three groups of measurements with mean temperatures of approximately $-30°$, $+40°$, and $+90°$ C.

The data of each group were adjusted to a common temperature by using the observed temperature dependence of the heat capacity. The adjustments were so small that they introduced no appreciable error. The original data and the heat capacities, before and after adjustment for temperature, are given in table 1, and in figure 3 the adjusted data are plotted.

TABLE 1.—*Heat capacities of oxygen* [1]

Mass of material	Mean temperature	Mean pressure	Temperature rise	Pressure drop in calorimeter	Joule-Thomson temperature fall	Flow rate	Power	$\frac{\Delta T}{W}$	C_P	C_P adjusted to temperature, t
g	° *C*	mmHg	° *C*	mm Hg	° *C*	*g sec*$^{-1}$	*Watt*	° *C watt*$^{-1}$	*cal mole*$^{-1}$ ° *C*$^{-1}$	*cal mole*$^{-1}$ ° *C*$^{-1}$ $t=-30°$ C
31.680	−29.75	764	10.468	20	0.007	0.021999	0.21085	49.7	6.999	6.998
38.505	−29.83	768	10.297	20	.007	.022181	.20883	49.3	6.989	6.989
16.390	−29.91	775	10.131	21	.007	.022764	.21107	48.0	6.996	6.996
32.047	−29.68	791	10.602	134	.047	.059226	.57666	18.5	6.994	6.993
32.583	−29.78	783	10.390	140	.048	.060331	.57563	18.1	6.992	6.992
43.540	−29.28	799	11.389	139	.048	.060472	.63222	18.1	6.992	6.991
60.774	−30.01	798	9.880	263	.089	.084394	.76852	13.0	6.988	6.988
50.680	−30.03	798	9.849	265	.089	.084462	.76808	12.9	7.000	7.000
60.841	−29.99	790	9.920	267	.090	.084503	.77303	12.9	6.991	6.991
										$t=40°$ C
25.885	39.61	757	9.124	8	.002	.011524	.09719	93.9	7.069	7.069
22.040	39.69	750	9.291	21	.006	.019357	.16595	56.0	7.054	7.054
24.763	39.62	751	9.158	21	.006	.019649	.16585	55.3	7.046	7.047
46.538	39.90	737	9.794	78	.024	.038328	.34659	28.3	7.045	7.045
56.005	39.89	763	9.682	141	.043	.052962	.47506	20.5	7.055	7.055
41.337	40.21	796	10.338	138	.041	.053000	.50688	20.5	7.049	7.049
70.156	40.21	796	10.311	138	.041	.053096	.50637	20.4	7.048	7.047
65.746	40.39	812	10.772	179	.055	.061240	.61030	17.7	7.041	7.040
67.440	39.93	780	9.860	217	.066	.066652	.60926	16.3	7.044	7.044
46.571	40.02	765	9.952	249	.072	.070601	.65213	15.4	7.049	7.049
47.046	41.54	773	13.001	251	.072	.071256	.85924	15.2	7.056	7.054
64.210	39.96	768	9.841	253	.073	.071351	.65223	15.2	7.053	7.053
51.428	39.95	767	9.823	254	.074	.071467	.65182	15.2	7.049	7.049
										$t=90°$ C
25.275	89.30	738	8.690	12	.004	.013242	.10713	81.2	7.118	7.119
34.818	89.80	720	9.686	22	.007	.018055	.16281	59.5	7.116	7.116
26.573	89.73	732	9.542	51	.015	.028250	.25131	38.0	7.120	7.121
36.511	89.58	765	9.162	48	.016	.028299	.24165	38.0	7.117	7.118
55.485	89.68	760	9.462	92	.027	.039132	.34578	27.4	7.123	7.124
45.422	89.86	771	9.794	91	.027	.039432	.36091	27.2	7.129	7.129

[1] One calorie is defined as 4.1833 Int. J.

2. Heat Leak

The heat leak of the calorimeter was determined by measuring heat capacities at varying flow rates, but the leak was found to be so small that no correction was made. The smallness of the leak is confirmed by heat transfer calculations

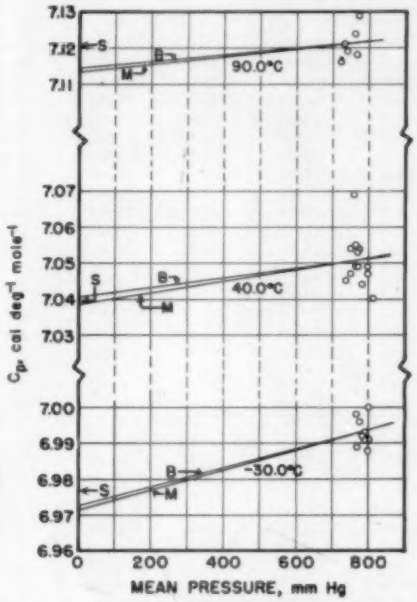

FIGURE 3.—*Experimental results for oxygen.*

B, Beattie-Bridgeman equation; *M*, Meyers equation; *S*, Spectroscopic value.

and especially by the agreement between the spectroscopic and experimental values for oxygen.

3. Comparison of the Experimental and Spectroscopic Heat Capacities

In order to compare the observed heat capacities with those calculated from spectroscopic data, it is necessary to obtain $C_P - C_P^\circ$. This was calculated by means of the general thermodynamic relationship

$$C_P - C_P^\circ = \int_0^P T(\partial^2 V/\partial T^2)_P dP, \qquad (2)$$

and with the aid of the Beattie-Bridgman equation [2] and an equation[2] developed by Meyers [3] especially for oxygen.

The effect of the reduction to the ideal gas state may be seen both in table 2 and figure 3, in which the experimental averages of $C_{P,\text{real}}$ are reduced to the ideal gas state and compared with the spectroscopic values. In table 2, groups of heat-capacity data are adjusted to a common pressure as well as temperature in order to facilitate comparison of the data. It may be seen that the experimental and spectroscopic values of the heat capacity agree within 0.04, 0.02, and 0.11 percent at −30°, +40°, and +90° C, respectively.

TABLE 2.—*Comparison of measured and spectroscopic values of the heat capacity of oxygen* [1]

Temperature	Mean C_P for 1 atm	C_P° calculated from column 2 by using $C_P - C_P^\circ$ from—		C_P° derived from spectroscopic data [2]
		Meyers equation	Beattie-Bridgeman equation	
° C	cal mole^{-1} ° C^{-1}	cal mole^{-1} ° C^{-1}	cal mole^{-1} ° C^{-1}	cal mole^{-1} ° C^{-1}
−30	6.993	6.972	6.973	6.976$_5$
40.04	7.050	7.038	7.040	7.039$_6$
90	7.121	7.113	7.114	7.120$_9$

[1] One calorie is defined as 4.1833 int. j.

[2] These values are obtained by interpolation in an unpublished table prepared by H. W. Woolley of the National Bureau of Standards, in which he has adjusted Johnston and Walker's [19] values for more recent values of the vibrational frequency [20], the radiation constant c_2 (1.4284 cm ° C^{-1}) and the gas constant (1.98714 cal mole^{-1} ° C^{-1}).

V. Results of Measurements on Isobutane and 1-Butene

1. Observed Data

The data for isobutane and 1-butene are presented in table 3 and in figures 4 and 5. Observations were made at two or more pressures, except for the data on 1-butene at 90° C. At −30° C the measurements on isobutane were made at rather low pressures to avoid condensation of the gas as it passed through the calorimeter. The computations follow the plan used for oxygen (section IV).

[2] $PV/RT = 1 + BV^{-1} + CV^{-2} + EV^{-4}$, where the coefficients B, C, and E have the values B, $-0.006772\,T_c(1-10^{-0.5032(T_c/T)}) + 0.0009878$; C, $4.2\times10^{-6}\,\frac{T_c}{T}(1-10^{-0.5032(T_c/T)}) + 1.426\times10^{-6}$; E, $-7.35\times10^{-12}\,\frac{T_c}{T}(1-10^{-2.5700(T_c/T)^2}) - 5.55\times10^{-12}$.

TABLE 3.—*Heat capacities of isobutane and 1-butene* [a]

Mass of material	Mean temperature	Mean pressure	Temperature rise	Pressure drop in calorimeter	Joule-Thomson temperature fall	Flow rate	Power	$\frac{\Delta T}{W}$	C_P	C_P adjusted to temperature, t
ISOBUTANE										
g	$°C$	mm Hg	$°C$	mm Hg	$°C$	$g\ sec^{-1}$	*Watt*	$°C\ watt^{-1}$	$cal\ mole^{-1}\ °C^{-1}$	$cal\ mole^{-1}\ °C^{-1}$
										$t=-30°$ C
24.380	−29.96	90	10.146	74	0.186	0.020309	0.29860	34.6	19.770	19.767
27.160	−29.97	94	9.980	78	.194	.020618	.29862	34.1	19.779	19.777
18.421	−30.05	91	9.949	76	.190	.020798	.30021	33.8	19.780	19.783
14.258	−29.95	180	10.047	18	.051	.013766	.19912	50.7	19.901	19.898
17.384	−29.99	178	9.978	18	.051	.013800	.19828	50.6	19.905	19.905
19.070	−30.00	179	9.964	18	.051	.013832	.19838	50.5	19.897	19.897
14.599	−30.06	180	9.824	48	.126	.022123	.31468	31.6	19.862	19.866
23.985	−30.03	176	9.868	47	.125	.022208	.31749	31.5	19.876	19.877
20.839	−29.96	178	10.042	84	.207	.030139	.44247	23.2	19.901	19.898
31.172	−29.99	180	9.973	85	.209	.030498	.44451	22.9	19.888	19.888
30.058	−30.07	176	9.826	96	.230	.030754	.44304	22.7	19.858	19.862
19.094	−29.99	233	9.938	36	.098	.022179	.31949	31.4	19.941	19.941
16.014	−29.91	228	10.071	36	.098	.022206	.32532	31.3	19.962	19.954
19.723	−29.91	227	10.080	36	.098	.022283	.32543	31.3	19.935	19.927
										$t=0°$ C
13.664	.11	189	10.211	29	.055	.016868	.26982	38.0	21.649	21.642
13.194	.09	189	10.178	29	.055	.016917	.26992	37.9	21.662	21.657
15.337	−.06	378	9.870	6	.013	.011343	.17600	56.2	21.812	21.817
12.267	−.02	390	9.868	6	.013	.011498	.18019	55.4	21.814	21.815
14.252	−.06	378	9.859	14	.028	.016964	.26312	37.6	21.796	21.800
14.754	−.13	390	9.748	29	.055	.024585	.37803	25.9	21.780	21.799
23.247	.06	380	10.093	40	.075	.028407	.45294	22.4	21.786	21.782
19.116	−.08	390	9.847	39	.073	.028605	.44517	22.3	21.796	21.801
										$t=40°$ C
12.979	39.78	184	9.568	36	.044	.017248	.28816	33.4	24.148	24.162
10.882	39.83	189	9.667	36	.044	.017250	.29124	33.3	24.155	24.166
13.213	40.23	389	10.451	8	.010	.011584	.21151	49.5	24.249	24.235
15.992	40.22	390	10.445	8	.010	.011587	.21151	49.4	24.258	24.244
18.051	40.04	387	10.082	15	.019	.016276	.28692	35.2	24.247	24.244
16.144	40.04	390	10.081	15	.019	.016290	.28701	34.8	24.235	24.233
41.364	40.33	387	10.662	61	.072	.032812	.61531	17.4	24.272	24.251
42.594	40.01	390	10.026	61	.072	.033065	.58258	17.3	24.241	24.241
										$t=80°$ C
14.886	79.72	185	9.439	22	.021	.012845	.23368	40.5	26.718	26.736
10.715	79.65	190	9.305	23	.021	.013201	.23696	39.4	26.740	26.763
14.054	79.64	391	9.272	22	.021	.018804	.33661	27.6	26.763	26.785
19.178	79.65	391	9.299	22	.021	.018811	.33784	27.6	26.772	26.795
28.436	80.30	387	10.604	56	.046	.029578	.60819	17.5	26.824	26.804
20.911	79.73	392	9.463	57	.047	.030230	.55438	17.2	26.792	26.809
18.226	79.72	391	9.431	58	.048	.030351	.55447	17.1	26.777	26.795
1-BUTENE										
										$t=40.4°$ C
10.632	40.43	372	10.874	6	0.008	0.009763	0.17126	63.5	21.619	21.615
24.495	40.52	371	11.050	14	.020	.015402	.27438	40.3	21.583	21.576
36.162	40.41	367	10.845	39	.054	.025733	.45110	24.2	21.571	21.571
62.818	40.34	369	10.703	99	.131	.041426	.72207	15.0	21.578	21.580
30.343	40.34	749	10 905	12	.016	.020285	.35944	30.4	21.790	21.763
41.559	40.35	747	10.920	23	.031	.028309	.50298	21.8	21.760	21.763
72.130	40.46	748	11.149	46	.062	.040318	.73372	15.3	21.771	21.768
67.243	40.44	749	11.091	98	.128	.059892	1.09059	10.3	21.768	21.765
										$t=90.1°$ C
16.148	89.97	754	9.867	4	.004	.010892	.19503	50.6	24.328	24.335
25.067	90.14	749	10.200	12	.010	.018669	.34582	29.5	24.332	24.330
55.472	90.18	748	10.288	50	.044	.039031	.73217	14.1	24.350	24.346
100.234	90.04	748	9.991	102	.089	.059021	1.02485	9.8	24.340	24.343

[a] One calorie is defined as 4.1833 int. j. The molecular weight of isobutane was taken as 58.120, and that of 1-butene as 56.104.

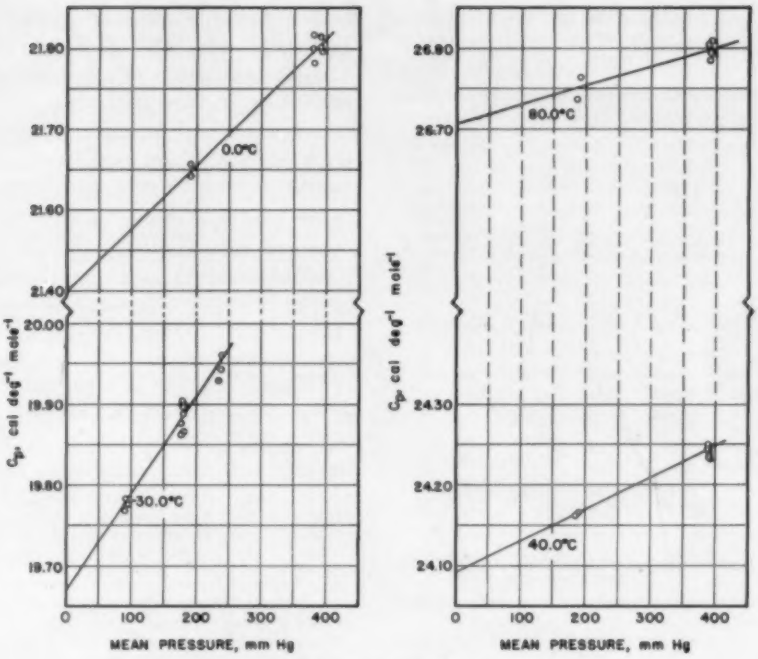

FIGURE 4.—*Experimental results for isobutane.*

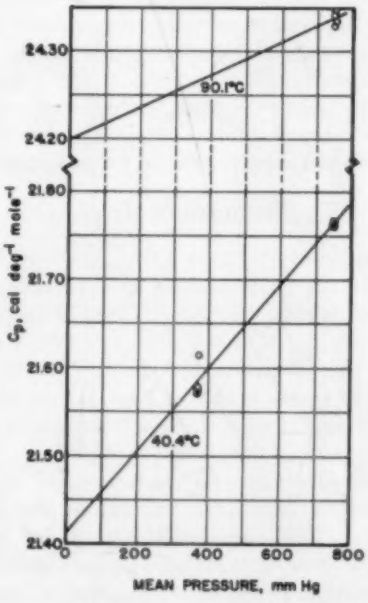

FIGURE 5.—*Experimental results for 1-butene.*

2. Reduction of the Specific Heat to the Ideal Gas State

(a) Isobutane

In order to obtain $C_P°$, the heat capacity data for a given temperature were plotted against pressure and extrapolated linearly to zero pressure (fig. 4). The results are given in column 6 of table 4.

Waddington, Todd, and Huffman [4], who determined the heat capacity of *n*-heptane and 2,2,3-trimethylbutane, also extrapolated their data linearly to obtain $C_P°$ values.

Values of $C_P - C_P°$ obtained by extrapolation are considered the most reliable; however, for the purposes of comparison, column 4 of table 4 gives the values of $C_P°$ obtained by using published critical constants [5] in the Berthelot equation, and column 5 gives the values of $C_P°$ obtained by using the constants of Benedict, Solomon, and Rubin [6] in their Kellogg equation. The experimental data used to determine the constants of the Kellogg equation consisted of measurements

of the liquid-vapor equilibrium in the methane-ethylene-isobutane system.

TABLE 4.—*Heat capacities of isobutane in the real and ideal states* [1]

Temperature	Pressure	Mean [2] $C_{P,\,real}$	$C_P°$ calculated from column 3 by using $C_P-C_P°$ from—			$(\partial^2V/\partial T^2)_P$ from heat capacity measurements
			Berthelot equation [2]	Kellogg equation [3]	Heat-capacity measurements	
°C	mm Hg	cal mole^{-1} °C^{-1}	cal mole^{-1} °C^{-1}	cal mole^{-1} °C^{-1}	cal mole^{-1} °C^{-1}	liter mole^{-1} °C^{-2}
−30	92	19.777	19.699	19.657		
−30	178	19.886	19.735	19.653	19.669	$15_2\times10^{-6}$
−30	229	19.940	19.745	19.641		
0	189	21.650	21.537	21.490		
0	384	21.802	21.572	21.476	21.503	8_9
40	186	24.165	24.091	24.071		
40	389	24.242	24.087	24.046	24.095	3_5
80	188	26.750	26.698	26.689		
80	390	26.797	26.689	26.671	26.706	2_1

[1] One calorie is defined as 4.1833 int. J, and the molecular weight of isobutane is taken as 58.120.

[2] The values of C_P were adjusted to the indicated temperatures and then averaged to facilitate correlation.

[3] These values were computed for comparison only. The values in column 6 are considered most reliable.

Values of $(\partial^2V/\partial T^2)_P$ were calculated from the change with pressure of the calorimetrically determined heat capacities by means of eq 2, assuming that $C_P-C_P°$ is proportional to pressure. The results are presented in column 7 of table 4.

(b) 1-Butene

For 1-butene at 40.4° C, the correction to the ideal gas state was assumed to be proportional to the pressure and $C_P°$ was obtained from calorimetric data by extrapolation to zero pressure (column 7 of table 5) as was done for isobutane. This procedure was chosen because the published data of state for 1-butene are more inadequate than for isobutane. To show the inadequacy of the equations of state for calculating reliable values of $C_P-C_P°$, columns 4, 5, and 6 were included in table 5 giving the values of $C_P°$ obtained with the Berthelot equation [7, 8], Meyers equation for the density of saturated vapors [9, 10, 11], and a previously used [12, 13] empirical equation.

$$PV/RT=1-k/VT^2. \qquad (3)$$

The value of k was estimated as 1.01×10^{-6} ml deg^2 g^{-1} from the vapor density data of Roper [14] and of Aston, Fink, Bestul, Pace, and Szasz [15]. It may be seen that the values of $C_P°$, calculated with the equations of state, vary more with pressure than is consistent with the accuracy of the calorimetric data. The recently published P-V-T data of Olds, Sage, and Lacey [16] are not sufficiently precise to give good values of $(\partial^2V/\partial T^2)_P$.

TABLE 5. *Heat capacities of 1-butene in the real and ideal states* [1]

Temperature	Pressure	Mean,[2] $C_{P,\,real}$	$C_P°$ calculated from column 3, using $C_P-C_P°$ from—				$(\partial^2V/\partial T^2)_P$ from heat capacity measurements
			Berthelot equation [4]	Meyers equation [4]	Equation 3 [4]	Heat capacity measurements	
°C	mm Hg	cal mole^{-1} °C^{-1}	cal mole^{-1} °C^{-1}	cal mole^{-1} °C^{-1}	cal mole^{-1} °C^{-1}	cal mole^{-1} °C^{-1}	liter mole^{-1} °C^{-2}
40.4	370	21.586	21.439	21.458	21.452		
40.4	748	21.765	21.468	21.498	21.487	21.411	$4_9\times10^{-6}$
90.1	750	24.338	24.146	.....	24.162	[3] 24.19	

[1] One calorie is defined as 4.1833 int. J and the molecular weight of 1-butene is taken as 56.104.

[2] This value was calculated as described in section V-2-b.

[3] The values of C_P were adjusted to the indicated temperatures and then averaged to facilitate correlation.

[4] These values were computed for comparison only. They indicate that the equations of state are not adequate for determining the correction to the ideal gas state.

At 90.1° measurements of C_P were made only at 750 mm Hg, and so the correction cannot be determined by extrapolation of the calorimetric data to zero pressure. The correction for 1-butene at 90.1° was computed from that at 40.4°, assuming that the ratio of the two corrections was the same as that found experimentally for isobutane.

VI. Estimate of Accuracy

As shown in section IV-3, the experimental values of the heat capacity of oxygen agree with those calculated from spectroscopic data within 0.04, 0.02, and 0.11 percent at −30°, +40°, and +90°C, respectively. If there is no significant difference between the relative accuracies of the data for oxygen and the hydrocarbons, and there is no evidence for such a difference, then the probable error of the mean values of $C_{P,\,real}$ presented in this paper should be roughly 0.07 percent. This value is in agreement with the probable error of 0.06 percent estimated from a consideration of the known sources of error.

VII. Comparison With the Work of Other Observers

A search of the literature failed to show either experimental heat-capacity data for oxygen with an accuracy comparable with that of the present measurements or reliable experimental heat-capacity data for 1-butene.

The heat capacity of isobutane has been measured by Dailey and Felsing [17] and by Sage, Webster, and Lacy [18]. The results of Dailey and Felsing agree with those obtained in this investigation within their estimated error (up to 1 percent) in the temperature range covered by both investigations. The values of Sage, Webster, and Lacey fall considerably below the results of this investigation and that of Dailey and Felsing. The data of the former were reduced to the ideal gas state with the Berthelot equation, but any error in the equation would be small in comparison with the differences between their data and those reported here. All the data for isobutane are presented in figure 6.

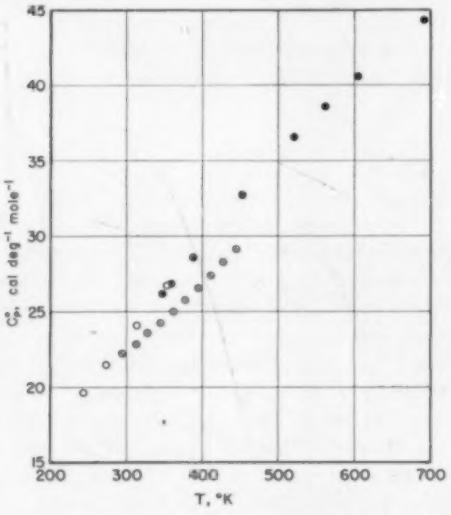

FIGURE 6.—*Comparison of results for isobutane with those of other investigators.*

●, Dailey and Felsing; ⊙, Sage, Webster, and Lacey; ○, this investigation.

VIII. References

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Heats of Solution of Solid Solutions of Hexacalcium Dialumino Ferrite and Dicalcium Ferrite

By Edwin S. Newman

The heats of solution of members of the series of solid solutions between $6CaO.2Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ have been determined. Members of this solid-solution series are formed in cement clinker instead of the single compound $4CaO.Fe_2O_3.Al_2O_3$, as formerly assumed. It has been shown that this assumption causes a negligible error in the latent heats at present used in estimating the glass content of portland cement clinker. It is pointed out, however, that the compositions and heats of solution of the glasses actually formed in portland cement clinker are still unknown. These quantities must be determined before the accurate estimation of the phase composition and glass content of commercial portland cement clinker is possible.

I. Introduction

For many years an objective of research on portland cement has been the correlation of the properties of the cements with their chemical constitution. This correlation requires the determination of the compositions of the mineral compounds in portland cement and the development of methods of calculating the relative amounts of each of these from the results of chemical analyses. Although notable progress has been made, errors in the estimates of the relative amounts of the minerals sometimes are large. These errors are partly due to inaccuracies in the estimate of the amount of glass, some of which is always present in portland cement. The determination of the glass content is based, in part, on values of the heats of solution of the individual minerals. The estimated glass content, therefore, will be in error unless the true substances present are recognized.

Recently there was announced the discovery in the ternary system CaO-Al_2O_3-Fe_2O_3 of a compound [1][1] hexacalcium dialumino ferrite, $6CaO.2Al_2O_3.Fe_2O_3$. There was also found a complete series of solid solutions having the general formula $6CaO.xAl_2O_3.yFe_2O_3$, in which x varies from two to zero and y simultaneously varies from one to three, the sum of x and y being always three. The extent of solid solution and the existence of the compound were unknown when many investigations of the constitution of portland cement clinker were made. As a first step in the possible revision of the method for the estimation of the glass content of portland cement clinker [2], the heats of solution in acid of the members of the solid-solution series have been determined.

[1] Figures in brackets indicate literature references at the end of this paper.

II. Materials, Procedure, and Apparatus

The raw materials used in this study were reagent-quality chemicals: low-alkali calcium carbonate, ferric oxide, and hydrated alumina. Two mixtures were prepared which would have, after ignition, the compositions $6CaO.2Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$. These basic mixtures were analyzed and their compositions adjusted. Quantities of these two materials were combined to give samples of about 10 g each of six other members in the solid-solution series. The samples, including those of the basic mixtures, were heated at 1,300°

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C and ground in an agate mortar. This treatment was repeated until formation of the compounds was judged complete when the samples were examined under the petrographic microscope. After the final heating, the unground samples were stored in screw-cap vials in a desiccator. Just prior to the determination of the heat of solution, each sample was ground in a power-driven mortar for periods of from ½ to 2 hours.

The heats of solution were determined in a mixture of nitric and hydrofluoric acids. Ten milliliters of 48 percent HF were used together with sufficient 2.500 N HNO_3 to make a total weight of 648.5 g. The heat-of-solution calorimeter used in this work has been described in detail elsewhere [3]. The methods of calculation of heats of solution were those used in precision calorimetry [4].

III. Results and Discussion

The heats of solution and the compositions of the samples are given in table 1. The compositions are given in weight percentages of $6CaO.2Al_2O_3$. Fe_2O_3 and $2CaO.Fe_2O_3$. It was found that when plotted as a function of composition, the values of the heats of solution lay along a straight line (fig. 1). Average values only are shown in figure 1, as many of the determinations gave heats of solution too close together to plot individually.

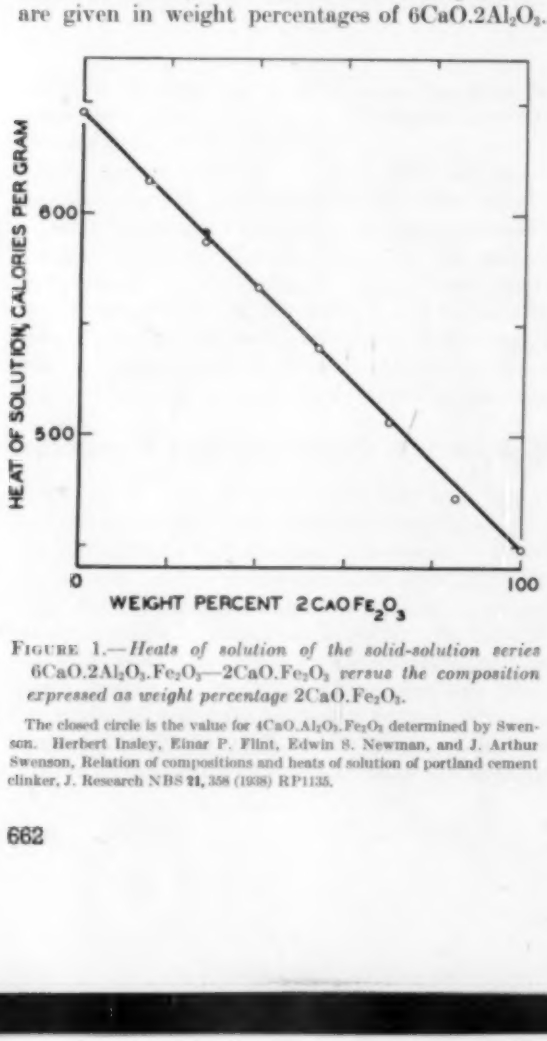

FIGURE 1.—*Heats of solution of the solid-solution series* $6CaO.2Al_2O_3.Fe_2O_3$—$2CaO.Fe_2O_3$ *versus the composition expressed as weight percentage* $2CaO.Fe_2O_3$.

The closed circle is the value for $4CaO.Al_2O_3.Fe_2O_3$ determined by Swenson. Herbert Insley, Einar P. Flint, Edwin S. Newman, and J. Arthur Swenson, Relation of compositions and heats of solution of portland cement clinker, J. Research NBS **21**, 358 (1938) RP1135.

TABLE 1.—*Compositions and heats of solution of members of the solid-solution series* $6CaO.2Al_2O_3.Fe_2O_3$—$2CaO.Fe_2O_3$

Composition		Compound formula	Heat of solution
$6CaO-2Al_2O_3-Fe_2O_3$	$2CaO-Fe_2O_3$		
wt percent	*wt percent*		*cal/g*
100	0	$6CaO-2Al_2O_3.Fe_2O_3$	647.2, 642.2, 646.2, 645.4, 646.6
			avg 645.5
85	15		615.8, 614.5, 615.0
			avg 615.1
72.0	28.0	$4CaO.Al_2O_3.Fe_2O_3$	587.6, 587.6, 586.7
			avg 587.1
60	40		566.2, 566.8, 566.3
			avg 566.4
46.2	53.8	$6CaO.Al_2O_3.2Fe_2O_3$	539.9, 538.8
			avg 539.4
30	70		506.8, 506.2, 506.1, 505.4
			avg 506.1
15	85		471.4, 473.2, 470.6
			avg 471.7
0	100	$2CaO.Fe_2O_3$	446.0, 448.3, 450.5, 448.7, 449.2, 450.6, 449.5
			avg 449.0

The equation $H=6.46C_6A_2F+4.49C_2F$ represents the straight line chosen to portray the weighted data. In this equation, H is the heat of solution in calories per gram of any member of the solid-solution series and C_6A_2F and C_2F represent the composition of this member in percentages of $6CaO.2Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$, respectively. This equation represents a line nearly parallel to the line of least squares and is drawn through the heats of solution of $6CaO.2Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$. This line approaches Swenson's value [5] for $4CaO.Al_2O_3.Fe_2O_3$, determined with this calorimeter, somewhat more closely than does the least-squares line of the present data.

Many calculations have been made of the constitution and the heats of solution of cement clinkers [5], assuming complete crystallization into the compounds $3CaO.SiO_2$, $2CaO.SiO_2$, $4CaO.Al_2O_3.Fe_2O_3$, and $3CaO.Al_2O_3$. Frequently the calculations were made after correcting the CaO for uncombined lime [6]. The heats of solution thus calculated often agreed with the experimentally determined heats of solution of the incompletely crystallized clinker. Consequently, the calculated compound composition was sometimes incorrectly taken to represent the actual constitution of the clinker. The heats of solution of several of the compounds are relatively close. Incorrect assumptions as to the crystalline substances present in the clinker, therefore, can often appear to be verified by agreement between the observed and calculated heats of solution.

For example, clinker 25F in table 4 of the paper by Lerch and Brownmiller on the estimation of glass [2] had an oxide composition of 63.3 percent of CaO, 5.0 percent of MgO, 5.9 percent of Al_2O_3, 3.2 percent of Fe_2O_3, and 22.2 percent of SiO_2. The heat of solution of an "annealed," i. e., completely crystallized, sample was 631.9 cal/g, determined experimentally. The calculated value, based on the incorrect assumption that the four compounds named in the preceding paragraph, together with MgO, were the constituents, was 632.9 cal/g. If these values were the results of actual duplicate determinations of the heat of solution with the vacuum-flask calorimeter [7], they would be considered in excellent agreement [8]. However, if the heat of solution is calculated on the basis that $6CaO.2Al_2O_3.Fe_2O_3$ is formed, as demonstrated by Swayze [1], instead of $4CaO.Al_2O_3.Fe_2O_3$, the value 630.4 cal/g is obtained. This value is also in excellent agreement with the experimentally determined value, although the calculated amounts of $3CaO.Al_2O_3$ and $2CaO.SiO_2$ have been decreased by 5.5 and 3.5 percent, respectively. Furthermore, the amount of $3CaO.SiO_2$ has been increased by 4.3 percent, and 14.0 percent of $6CaO.2Al_2O_3.Fe_2O_3$ having a heat of solution of 642 cal/g [2] has been substituted for 9.7 percent of $4CaO.Al_2O_3.Fe_2O_3$ having a heat of solution of 587 cal/g.

Because of the formation of $6CaO.2Al_2O_3.Fe_2O_3$ instead of $4CaO.Al_2O_3.Fe_2O_3$, the latent heats of crystallization of the liquids studied by Lerch and Brownmiller [2] are slightly in error. This difference is caused by the formation at crystalline equilibrium of different amounts of $2CaO.SiO_2$ than assumed in their work. The observed differences between the heats of solution of the glasses and of the same material at crystalline equilibrium are the sums of the latent heats of the glasses plus the heat effects of the beta-to-gamma inversion of dicalcium silicate. The corrections to the observed differences in heats of solution to give the latent heats are therefore somewhat different than calculated by Lerch and Brownmiller [2].

The potential compound compositions at crystalline equilibrium and the heats of solution were recalculated for the nine liquid compositions given in reference [2]. The recalculated heats of solution agreed as well with the observed heats of solution as did those calculated on the former basis, the root-mean-square deviation being 1.7 cal/g compared with 2.1 cal/g. The differences in the calculated amounts of $2CaO.SiO_2$ caused small differences in the latent heats of the glasses, amounting in the largest case to about 1.5 percent. Errors introduced from this cause into the estimation of the glass content of portland cement clinkers are insignificant compared with the normal errors of such calorimetry and with the errors introduced by the present lack of knowledge of the true composition of these glasses.

At present, the composition relations between the solid solutions of $6CaO.2Al_2O_3Fe_2O_3$—$2CaO.Fe_2O_3$ and the liquids in equilibrium with them are not known. It is therefore not possible to

[2] The heat of solution of $4CaO.Al_2O_3.Fe_2O_3$ in the calorimeter used in the present work was 591 cal/g, differing from the value given in reference [2] by 4 cal/g. The value 646 cal/g for $6CaO.2Al_2O_3.Fe_2O_3$ obtained in the present investigation was therefore reduced by 4 cal/g in recalculating the heats of solution.

estimate the compositions and quantities of the liquids formed at equilibrium in the system $2CaO.SiO_2$—$5CaO.3Al_2O_3$—$2CaO.Fe_2O_3$—CaO—MgO. The heats of solution and latent heats of the glasses formed by cooling these liquids cannot be determined until their compositions are known. When this information is available, the phase composition and the glass content of commercial portland cement clinkers can be estimated more accurately than at present.

IV. Summary

The heats of solution of members of the series of solid solutions between $6CaO.2Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ have been determined. Members of this solid-solution series are formed in cement clinker instead of the single compound $4CaO.Fe_2O_3.Al_2O_3$ as formerly assumed. It has been shown that this assumption causes a negligible error in the latent heats at present used in estimating the glass content of portland cement clinker. It is pointed out, however, that the compositions and heats of solution of the glasses actually formed in portland cement clinker are still unknown. These quantities must be determined before the accurate estimation of the phase composition and glass content of commercial portland cement clinker is possible.

The author is indebted to Mario Storlazzi and Leonard Bean for the chemical analyses and to L. A. Dahl for assistance in computation.

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Relative Thickness of Lead, Concrete, and Steel Required for Protection Against Narrow Beams of X-Rays

By George Singer,* Harold O. Wyckoff, and Frank H. Day

The lead equivalents of X-ray protective barriers are given for both concrete and steel for potentials between 200 and 1,400 kv. These were determined experimentally using a pressure ionization chamber and an X-ray tube to which constant potential was applied. Narrow X-ray beams were used. The data obtained are compared with those published by other workers. Data on the relative masses referred to lead of both concrete and steel barriers are included. The agreement among the several laboratories is satisfactory when consideration is given to differences in the test specimens used and in the experimental technic.

It is the purpose of this paper to present experimental data on the relative thickness of lead, concrete, and steel needed for protection against narrow beams of X-rays generated by potentials between 200 and 1,400 kv and to compare these with similar results published by other laboratories. The total range so covered is 70 to 2,000 kv. The usefulness of such data depends upon the availability of information on the thickness of lead required for protective barriers. The American Standards Association Code Z54.1 [1] [1] contains such recommendations for potentials up to 250 kv. Details of the research leading to the recommended absorption curves for X-rays are given in other papers [2, 3]. Wide-angle X-ray beam absorption in concrete is also given for 1,000 and 2,000 kv. Other technical publications contain limited absorption-curve data for potentials up to approximately 2,000 kv as well as some data on the lead equivalent of various building materials [4 to 11, incl.].

I. Introduction

Concrete and steel have become important as materials for the construction of X-ray protective barriers; both are now used extensively to supplement metallic lead and its compounds in installations for X-rays generated by potentials up to approximately 400 kv and to replace, in large part, lead and its compounds in protective barriers for X-rays generated by voltages above this value. This trend, given additional impetus by war conditions that have made the procurement of metallic lead difficult and the construction of metallic barriers costly, is firmly established and is unlikely to be reversed as there are sound economic reasons to justify it. As the penetrating power of X-radiation is increased up to about 3,000 kv, the effectiveness of materials of relatively low effective atomic number—such as concrete, or steel—increases also; unlike lead, these materials do not require costly supporting structures. Most high-voltage X-ray installations are housed in new buildings of steel and concrete construction; the walls, ceilings, and floors in such buildings can be made adequately protective at relatively little additional cost by increasing their thickness sufficiently.

None of these papers covers the whole range of X-ray quality now commonly used in the medical and industrial applications; they are widely scattered in the literature, appearing in both English and German, and in scientific and technical journals to which designers of X-ray equipment and X-ray installations do not have ready access.

* Deceased.

[1] Figures in brackets indicate the literature references at the end of this paper.

Often protective barriers are located quite near the personnel that they are to protect, and the barriers are irradiated by X-rays over large areas. The new data presented in this paper do not apply under such conditions. Only when the barrier is located far from the personnel to be protected and the irradiated area is small should this new information be used. It has been theoretically predicted and experimentally verified that the difference in apparent absorption should be perceptible in the region where scattering is appreciable. In section IV–2 attention is called to some measurements that give the order of magnitude of this difference expressed in terms of the lead equivalent.

II. Test Specimens

Singer, Taylor, and Charlton [9] have reported that for narrow X-ray beams generated by potentials from 200 to 400 kv the lead equivalent of a concrete barrier is proportional to its density and is, for practical purposes, unaffected by the nature of the concrete mix, except as the composition affects the density of the concrete. Tests made in connection with the present study—the results of which are presented in a later section—confirm this finding for X-rays generated by potentials up to 1,400 kv for concrete and steel. As the lead equivalents of concrete barriers of different composition but of the same density are the same, it is sufficient to confine attention to specimens of but a single composition. Accordingly, only one concrete mix was examined. The specimens used are those described in reference [9]. Three sizes of concrete cylinders were used. Of these, the first is 15 cm in diameter and 11 cm in length; the second, 20 cm in diameter and 16 cm in length; and the third, 20 cm in diameter and 22 cm in length. The volume ratio of cement to sand to gravel is 1:2.2:3.8. Although the density of these specimens varies from 2.34 to 2.40 g/cm^3, all data relating to them have been corrected so as to apply to concrete of density 2.35 g/cm^3, that is, concrete weighing approximately 147 lb/ft^3. For further details, the original paper should be consulted.

The steel specimens consist of 30-cm squares of cold-rolled steel approximately 1.27 cm thick of density 7.8 g/cm^3.

III. Method

The method used in determining the lead equivalent of all specimens is essentially that described in the paper by Singer, Taylor, and Charlton [9]. It consists in comparing the X-ray attenuation due to each specimen with that due to each of a series of lead sheets of known thickness. This is done by measuring the relative ionization in a pressure ionization chamber when each specimen is used as a filter under identical operating conditions. The apparatus used is shown in figure 1. The X-ray generator has been described by E. E. Charlton and H. S. Hubbard [12]. This consists of a constant-potential power supply and a pumped X-ray tube made up in 10 sections. Power is supplied to the generator from a synchronous motor-generator set, the output voltage of which is remotely controlled by vary-

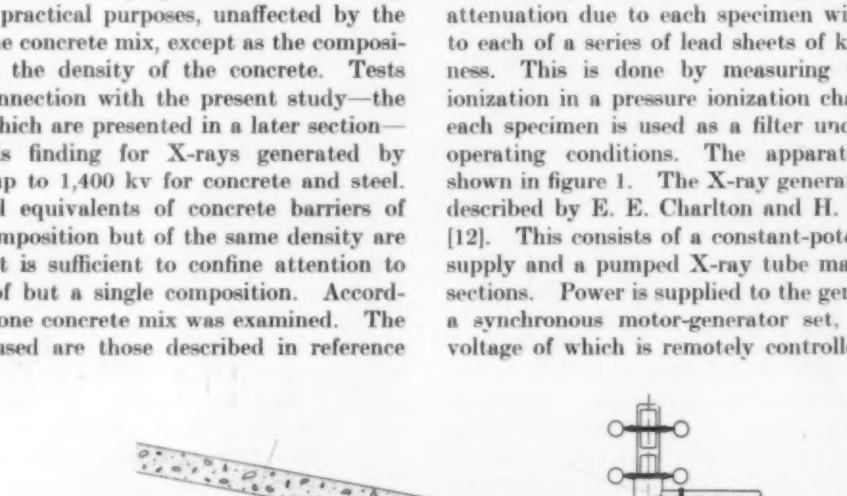

FIGURE 1.—*Cross section of apparatus used in determination of lead equivalent of concrete and steel.*

ing the resistance in series with the generator field winding. The constant potential applied to the tube is measured by means of a potentiometer used in conjunction with a wire-wound resistor of 1,400 megohms in parallel with the tube and its supply. It is conservatively estimated that by means of this voltmeter the tube voltage can be measured with an accuracy of better than 1 percent. As this voltmeter is a modification of the type described by Taylor for lower voltages, his paper [13] should be consulted for further details. The tungsten target of the X-ray tube is of the reflection type, that is, the axis of the X-ray beam is at right angles to the axis of the X-ray tube. The anode cylinder of this tube is surrounded by a shield, *B*, containing 4 in. of lead shot. The lead cylinder, *D*, immediately in front of the tube target, *A*, contains a monitoring ionization chamber used to check the constancy of the X-ray output. The lead diaphragm in the end of this cylinder limits the X-ray beam to a diameter of approximately 10 cm at the incident face of the first test specimens, *H*. Immediately in front of this diaphragm there are a 3-in. lead shutter, *F*, and a series of lead filters, *G*; both the shutter and the filter system are remotely operated from the control room. The test specimens were placed at a distance of from 1 to 2 m from the tube target. Beyond the specimens a temporary brick wall, *I*, 30 cm thick, was erected in order to reduce the effect of scattered radiation. The X-radiation passes through the aperture in this brick baffle, and after passing through the 4-cm aperture in the diaphragm, *J*, in front of the lead-shot baffle, *K*, enters the pressure ionization chamber. The ionization current produced within this chamber is amplified by an FP–54 amplifier and is measured by a potentiometer in the grid circuit of the amplifier. For details relating to the pressure ionization chamber and the ionization measuring system used, reference should be made to the paper by Taylor, Singer, and Charlton describing this apparatus [14].

No filtration was used other than that inherent in the X-ray tube and in the monitoring ionization chamber. This filtration consisted of 0.79-mm brass, 0.79-mm copper, 12.7-mm water, and 1.53-mm aluminum.

The experimental procedure is as follows: One or more of the test specimens are placed in the position indicated in figure 1, the number used at any one time depending upon the thickness of concrete for which the lead equivalent is desired. In this way, the concrete thickness is increased in steps of approximately 5 cm to a total sufficient to reduce the dosage rate to 0.35×10^{-5} r/sec or less for any given quality of radiation. At a given tube voltage and tube current the ionization current is determined by the measuring system described above. The specimens are then removed from the beam, and lead filters are introduced in turn by means of the remotely controlled filter system. This is continued until a combination of lead filters is found for which the ionization current is the same as that observed with the specimen in the beam. The total thickness of lead in the beam is taken to be the lead equivalent of the specimen in question. If no such combination of filters is available, the lead equivalent is found by means of an interpolation curve for lead filters having approximately the lead equivalent of the specimen. To find the thickness ratio in any given case, the thickness of the sample is divided by the thickness of its equivalent lead filter.

For purposes of X-ray protection, the lead equivalent of any sample, and therefore, the thickness ratio, should be determined for barriers of sufficient thickness to reduce the dosage rate of any given beam of radiation incident upon it to approximately 0.35×10^{-5}r/sec [2]; that is, to such a level that a person may remain behind the barrier continuously for 8 hr and receive no more than 0.1 r. When ionization measurements are carried out for barrier thicknesses sufficient to bring about such a reduction in the dosage rate of the incident radiation, scattering effects become important and must be eliminated, if possible, or if not possible, must be corrected for. In order to minimize the effect of scattering when very thick specimens are examined, ionization readings for each specimen and for each lead filter are taken in two steps: (1) as described above, and (2) with a 6-in. lead plug inserted in the aperture, *L*, in the 6-in.

[2] The tolerance dose was defined by The International X-ray and Radium Protection Commission at the Fifth International Congress of Radiology, Chicago, September 1937, as 0.2 roentgen per day, which "on the basis of continuous irradiation during a working day of 7 hours * * * corresponds to a tolerance dosage rate of 10^{-5}r/sec." As more and more penetrating radiation has come into common use in both medicine and industry, a trend has developed toward the reduction of the daily tolerance dose from 0.2 to 0.1 r. In both Handbook HB20 of the National Bureau of Standards and in the Industrial X ray Safety Standard of the American Standards Association, the daily tolerance, or permissible dose, is given as 0.1 r, which on the basis of continuous exposure throughout an 8-hr working day is equivalent to approximately 0.2 milliroentgen per minute, or 0.35×10^{-6}r/sec.

baffle, K. This second reading is a measure of the scattered radiation entering the pressure chamber. The ionization reading for the specimen or lead filter in question is found by taking the difference between the first and second of these readings.

IV. Results

1. Effect of Tube Voltage and Barrier Thickness

For concrete, the lead equivalent of each specimen was determined for potentials from 400 to 1,400 kv in steps of 100 kv. The results so obtained have been plotted in figure 2 to show the lead equivalent of concrete at each of these voltages as a function of the barrier thickness. For the sake of completeness, there has been added to these curves, others based on similar data published earlier by Singer, Taylor, and Charlton [9] for generating potentials between 200 and 400 kv. The increasing effectiveness of concrete as a protective barrier with increasing voltage, an effect that is very pronounced in the potential range between 200 and 400 kv, is still apparent at 1,400 kv, but the rate of this increase falls with increasing potential. For high generating potentials and for thick barriers, the curve showing the lead equivalent of a barrier as a function of its thickness is approximately linear. For low voltages and relatively thin barriers, the curves are parabolic.

In table 1 the results obtained for concrete are summarized for narrow X-ray beams. In the first column the voltage applied to the tube is given; in the second, the ratio of thickness of concrete to thickness of lead giving equivalent protection under identical conditions; in the third, the mass ratio, that is, the ratio of the mass of a concrete barrier to that of a lead barrier affording equivalent protection under identical conditions. In table 2 similar data are given for steel.

As the lead equivalent of a barrier material is not in general proportional to the barrier thickness, the thickness ratios given in the second column of tables 1 and 2 will depend upon the barrier thickness. The thickness of especial interest is that sufficient to reduce the intensity of the X-radiation incident upon it to the "tolerance" or "permissible dosage rate." For the purpose of computing the thickness ratios given in tables 1 and 2, it has been assumed that the barrier in question is such as to reduce to 10^{-5}r/sec the X-radiation incident upon it from an X-ray tube 1 m away when the tube is operated at the potential indicated and at a tube current of 3 ma. These factors were selected in order to facilitate comparison of these data with data reported by others for approximately the same conditions. Under other operating conditions, these ratios are still sufficiently accurate for practical purposes, since, as is evident from figure 2, the lead equiva-

TABLE 1.— *Thickness and mass ratios for concrete*

X-ray energy	Thickness ratio for concrete [1]	Mass ratio for concrete [2]
kv		
200	[3] 55	11.4
250	[3] 34	7.1
300	[3] 24.6	5.1
400	[3] 16.2	3.4
500	11.5	2.4
600	9.3	1.9
700	8.1	1.7
800	7.1	1.5
900	6.5	1.4
1,000	6.1	1.3
1,200	5.6	1.2
1,400	5.2	1.1

[1] The thickness ratio is obtained by dividing the thickness of concrete by the thickness of lead required for equal protection under identical conditions.

[2] The mass ratio is obtained by dividing the mass of a concrete barrier by the mass of a lead barrier required for equal protection under identical conditions.

These ratios are computed for a concrete barrier of sufficient thickness to reduce a narrow beam of incident radiation to 10^{-5}r/sec at 1 m from an X-ray tube operated at the voltage indicated and a tube current of 3 ma. All data were obtained at the National Bureau of Standards.

[3] G. Singer, L. S. Taylor, A. L. Charlton, J. Research NBS **21**, 783 (1938) RP1155.

TABLE 2.— *Thickness and mass ratios for steel*

X-ray energy	Thickness ratio for steel [1]	Mass ratio for steel [2]
kv		
200	13.6 [6]	9.4
300	7.5 [6]	5.2
400	4.9 [6]	3.4
500	3.5 [5]	2.4
600	2.9	2.0
800	2.2	1.5
1,000	1.9	1.3
1,400	1.7	1.2

[1] The thickness ratio is obtained by dividing the thickness of steel by the thickness of lead required for equal protection under identical conditions.

[2] The mass ratio is obtained by dividing the mass of a steel barrier by the mass of a lead barrier required for equal protection under identical conditions.

These ratios are computed for a steel barrier of sufficient thickness to reduce a narrow beam of incident radiation to 10^{-5}r/sec at 1 m from an X-ray tube operated at the voltage indicated and a tube current of 3 ma. Unless otherwise specified the data given are those obtained at the National Bureau of Standards.

lent of a barrier tends to become linear for barrier thickness of the order required for adequate X-ray protection. For this reason, tables 1 and 2 (and their graphs given in figures 3 and 4, respectively) may be used without appreciable error in computing X-ray protection for various tube currents and distances on the basis of a daily tolerance dose of 0.1 r (0.35×10^{-5}r/sec).

In figure 3 the thickness ratio for concrete has been plotted as a function of the tube voltage that applies. The heavy line through the open circles is that obtained for the data given in table 1, covering the potential range from 200 to 1,400 kv. In the interest of completeness, and for the purpose of comparison, points obtained from the published data of 11 other workers have also been plotted. With the exception of the data taken from Heidenreich and Jeager [4], the agreement between the several workers, although not as close as might be desired, is as good as can be expected when

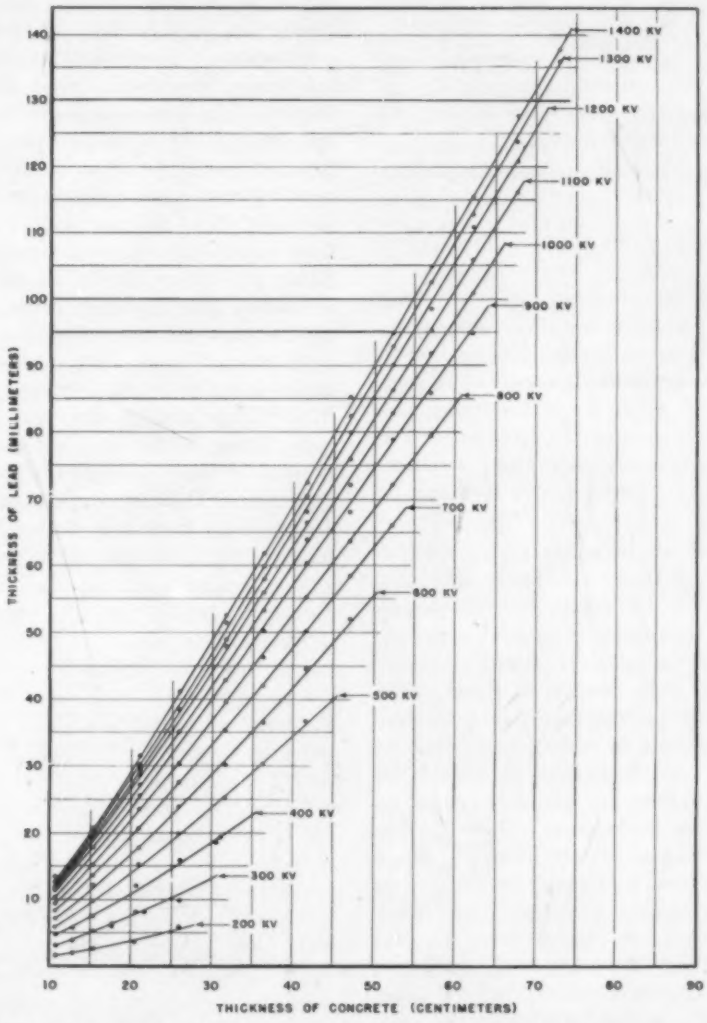

FIGURE 2.—*Variation of lead equivalent of a concrete barrier with barrier thickness for potentials between 200 and 1,400 kv.*

Lead equivalent of concrete, constant potential; narrow X-ray beam, axis at right angles to axis of electron stream; density of concrete 2.35 g/cm³.

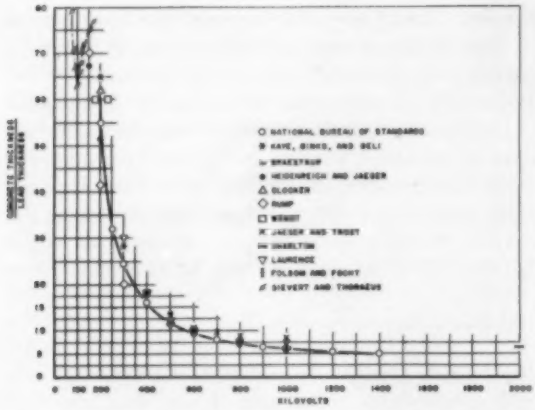

FIGURE 3.—*Ratio of concrete thickness to lead thickness as a function of tube voltage.*

Ratio of concrete thickness to lead thickness to reduce radiation at one meter to 10^{-5} r/sec.

consideration is given to all factors affecting the end result. Aside from the errors involved in the making of such measurements—of which only a rough estimate is possible—there are many conditions that are not equivalent for the several determinations. A significant comparison of such data is possible only when the test samples, the nature of the radiation, and the irradiated area are similar, and furthermore only when the accuracy with which these factors are defined can be specified.

Correction for differences in the test specimens is possible whenever their density is specified; likewise, correction for differences in initial dosage rate can be made if the necessary data are supplied. These corrections, being relatively simple to make, were applied to all data plotted in figure 3 for which the necessary information was available. The effect of variations in radiation quality on the results, while very important, is difficult to determine as many operating conditions must be considered in such an evaluation. These include the generator wave form; the accuracy of voltage measurement; the tube bias used, both inherent and controlled; the direction of the X-ray beam with respect to that of the electron stream; filtration; and spectral selectivity of the radiation detector used. While important at all voltages, these factors become increasingly so as the tube voltage is increased. In figure 3 no attempt was made to correct for any of the factors relating to the specification of radiation quality or beam diameter.

The results of all the laboratories clearly show the essential characteristics of protective barriers made of concrete or of similar materials of low atomic number. As already noted, such barriers are comparatively ineffective at low voltages; that is, a greater thickness ratio is, in general, required for soft X-rays than for X-rays of relatively greater penetrating power. Thus, at 200 kv a concrete barrier should be about 60 times as thick as a lead barrier if equivalent protection is to be had, whereas, at 1,000 kv, a comparable concrete barrier need be only about six times the thickness of its equivalent lead barrier. The discontinuity in the curve at approximately 100 kv is caused by the *K*-absorption limit of lead. As a result of this discontinuity, such barriers have a minor maximum lead equivalent at this voltage and a minor minimum lead equivalent at approximately 200 kv. For potentials above 200 kv the lead equivalent increases (the thickness ratio decreases) rapidly at first and then more slowly as the photoelectric absorption of lead becomes less important, until in the range between 1,000 and 2,000 kv relatively little change is to be observed.

In figure 4 the thickness ratios for steel are plotted to show variation with X-ray generating potential. These data were taken from table 2. In addition, there is included the thickness ratio of steel at 2,000 kv computed from absorption

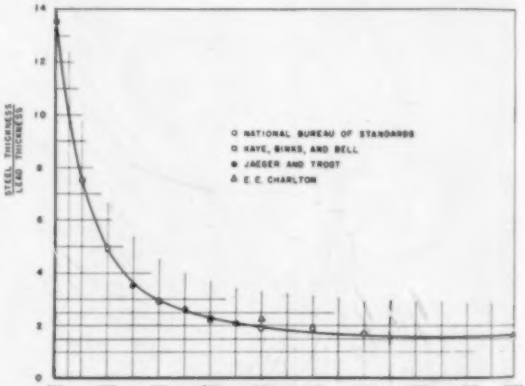

FIGURE 4.—*Ratio of steel thickness to lead thickness as a function of tube voltage*

Ratio of steel thickness to lead thickness to reduce radiation at one meter to 10^{-5} r/sec.

curves recently published by Charlton and Westendorp [10]. Except that the thickness ratios for steel are less than for concrete —approximately in the ratio of the densities of the two materials for this potential range—the discussion given in connection with figure 3 applies also to figure 4.

2. Effect of X-ray-Beam Diameter

The lead equivalent obtained for a given test sample depends upon the area of the sample irradiated in making the determination. Materials of low atomic number produce a larger percent of their X-ray attenuation by scattering than does lead whose photoelectric absorption is still appreciable in this potential range. Therefore, when determined for an X-ray beam of large diameter, the lead equivalent of a barrier of relatively low atomic number is less than that obtained when a small beam is used. The use of small fields is desirable because only under such experimental conditions can accurately reproducible data be obtained. This technic is objectionable, however, as a lead equivalent so obtained is not necessarily a true measure of the effectiveness of a given barrier under actual working conditions. When very broad beams are used, the actual lead equivalent of the barrier in question may be much less than indicated by experimental determination involving the use of small X-ray fields. This effect must be guarded against, especially for very penetrating radiation, as the effect becomes greater the more penetrating the radiation becomes. Unfortunately, because of technical difficulties in obtaining such data, there is at present relatively little information available on the effect of beam size.

Of the data on thickness ratios for concrete presented in graphical form in figure 3, only the points taken from the work of Jaeger and Trost [5], and also from Braestrup's [3] paper, were obtained with the broad beams encountered in the application of radiation barriers. The experimental conditions for which the work of Jaeger and Trost was carried out was such that the diameter of the beam is approximately 30 cm. The beam size in Braestrup's work is not specified. The differences between the lead equivalents obtained by these workers and those obtained by the others listed in figure 3 are therefore significant as they give a rough indication of the decrease in the lead equivalent of a barrier when different beam sizes are used.

3. Mass Ratio for Concrete and Steel

In the construction of new buildings for housing X-ray installations, the matter of the relative mass of various protective barriers must of course be considered in the design of the building, but this factor is of relatively greater importance when an X-ray installation is to be set up in an old building, in which serious restrictions may be imposed on the additional loading that may be applied to walls, floors, and ceilings without approaching the danger point. For use in connection with the problems of this nature, there is given in figure 5 the mass ratio of both steel and concrete barriers for potentials between 100 and 1,400 kv. Here, again, there is shown in addition to the data first reported here, that recomputed from the published work of several other workers in this field. It should be noted that the points for concrete and steel both fall on a single curve. This means that the lead equivalents of barriers

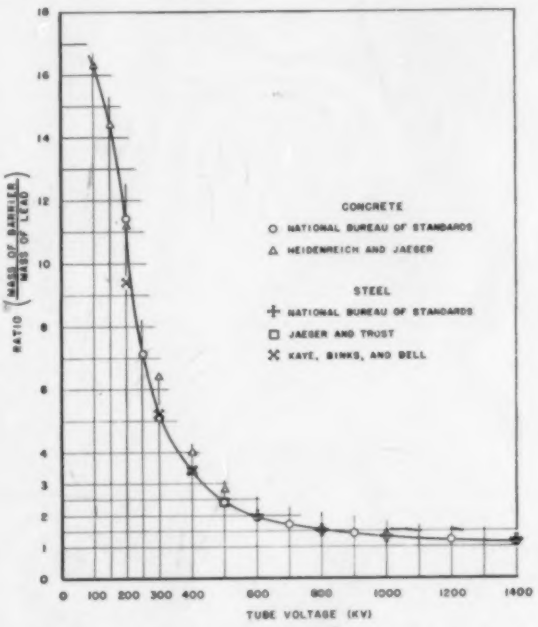

FIGURE 5.—*Mass ratio of concrete and steel barriers for potentials between 100 and 1,400 kv*

Mass ratio for concrete and steel barriers—narrow X-ray beam.

constructed of these materials are proportional to their relative densities.

V. Summary

Metallic lead is the primary X-ray protective material in the low-voltage range. It has been supplemented by such materials as concrete and steel in the supervoltage range but is unlikely to be entirely superseded. For this reason, the specifications of the relative effectiveness of various materials as protective barriers in terms of metallic lead is of interest. From the data presented herein for lead, concrete, and steel, it is possible to determine the thickness of a barrier of anyone of these materials when that for lead is known.[3] For potentials up to 250 kv, the recommendations of the American Standards Association are available. For X-rays generated by potentials greater than 250 kv, limited experimental and theoretical data for absorption curves are available, but there has been no general agreement on these requirements in the supervoltage region, except for the concrete curves for wide angle beams given by the ASA Code.[4]

[3] It is necessary that caution be used in such an application for the data given in this paper applies only to the case of narrow beams of X-rays.

[4] The National Bureau of Standards has recently completed an experimental arrangement for determination of the effect of the size of the irradiated area of the barrier upon the attenuation produced. It is expected that this information will soon be available.

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WASHINGTON, September 19, 1946.

INDEX TO VOLUME 38

A

Page

Absorption losses of a photographic lens, compensation of aperture ratio markings, RP1803 643
Acid-base titrations in nonpolar media, RP1794 527
Acree, S. F., Arthur A. Maryott, Dipole moments and resonance of some benzein indicators and related compounds, RP1791 505
Aircraft exhaust coatings, RP1773 293
Air flow along a flat plate, RP1772 251
Aliphatic hydrocarbons, preparation and properties, RP1779 365
Alkylates, analysis, RP1795 537
Alkylcyclohexanes, purification, purity, and freezing points, RP1760 53
Alkylcyclopentanes, purification, purity, and freezing points, RP1760 53
Aluminum alloy, effect of aging on some properties, RP1788 465
Aluminum oxide, heat capacity, RP1797 593
American Petroleum Institute-National Bureau of Standards hydrocarbons, RP1760 53
Annealing of glass, changes in refractivity and density, RP1793 519
Aperture ratio markings of a photographic lens, compensation for absorption, reflection, and vignetting losses, RP1803 643
Argon and krypton, infrared emission spectra, RP1790 499
Aromatic hydrocarbons, purification, purity, and freezing points, RP1760 53
Aviation fuel components, analysis, RP1795 537

B

Balcom, Margaret M., Kasson S. Gibson, Transmission measurements with the Beckman quartz spectrophotometer, RP1798 601
Barium-strontium titanate dielectrics, properties, RP1776 337
Beckman spectrophotometer, performance, RP1798 601
Bekkedahl, Norman, Waldemar Saffioti, Mangabeira latex and rubber, RP1785 427
Benzein indicators, dipole ments and resonance, RP1791 505
Benzene and dioxane, conductimetric titrations of acids and bases in, RP1794 527
Benzene hydrocarbons, purification, purity, and freezing points, RP1760 53
Beta-ray spectra of cobalts, RP1778 359
Bradt, Paul, A. Keith Brewer, Samuel L. Madorsky, John Keenan Taylor, Vernon H. Dibeler, O. Lee Parham, Roy J. Britten, J. Gilman Reid, Jr., Concentration of isotopes of potassium by the countercurrent electromigration method, RP1765 137
Brewer, A. Keith, Samuel L. Madorsky, Concentration of the isotopes of mercury by free evaporation in a 10-cell countercurrent reflux still, RP1764 129
—, *Samuel L. Madorsky, John Keenan Taylor, Vernon H. Dibeler, Paul Bradt, O. Lee Parham, Roy J. Britten, J. Gilman Reid, Jr.*, Concentration of isotopes of potassium by the countercurrent electromigration method, RP1765 137
Brick, refractory, creep and elastic behavior, RP1770 229
Britten, Roy J., A. Keith Brewer, Samuel L. Madorsky, John Keenan Taylor, Vernon H. Dibeler, Paul Bradt, O. L. Parham, J. Gilman Reid, Jr., Concentration of isotopes of potassium by the countercurrent electromigration method, RP1765 137
Brooks, Donald B., Frank L. Howard, Thomas W. Mears, A. Fookson, Philip Pomerantz, Preparation and physical properties of several aliphatic hydrocarbons and intermediates, RP1779 365
Bunsen ice calorimeter, RP1796 583
1-butene, heat capacities, RP1804 651
Butenes, vibrational frequencies, RP1768 191
Bunting, Elmer N., George R. Shelton, Ansel S. Creamer, Properties of barium-strontium titanate dielectrics, RP1776 337
Butylbenzenes, purification, purity, and freezing points, RP1760 53

C

Page

Cahill, Janice C., Anton J. Streiff, Evelyn T. Murphy, Helen F. Flanagan, Vincent A. Sedlak, Charles B. Willingham, Frederick D. Rossini, Purification, purity, and freezing points of 8 nonanes, 11 alkylcyclopentanes, 6 alkylcyclohexanes, and 4 butylbenzenes of the American Petroleum Institute-Standard and American Petroleum Institute-National Bureau of Standards series, RP1760 53
Calorimeter, Bunsen ice, RP1796 583
Calorimetry of gases, RP1804 651
Carbon monoxide, analysis of, RP1777 351
Cement, portland, spectrographic analysis, RP1786 439
Ceramic coatings for high temperature protection of steel, RP1773 293
Cheney, Ruth K., Paul F. Wacker, Russell B. Scott, Heat capacities of gaseous oxygen, isobutane, and 1-butene from −30° to +90° C, RP1804 651
Chlorine isotopes, concentration by the countercurrent electromigration method, RP1767 185
Coatings for steel at high temperatures, RP1773 293
Compensation of the aperture ratio markings of a photographic lens for absorption, reflection, and vignetting losses, RP1803 643
Concentration of isotopes of potassium by countercurrent electromigration.
RP1765 137
RP1766 169
Coder, Irvin L., Chauncey G. Peters, Walter B. Emerson, Karl Neffen, Frank K. Harris, Electrical methods for diamond-die production, RP1787 449
Corrosion of aluminum alloy, RP1788 465
Corruccini, Robert J., Defoe C. Ginnings, An improved ice calorimeter—the determination of its calibration factor and the density of ice at 0° C, RP1796 583
—, —, Enthalpy, specific heat, and entropy of aluminum oxide from 0° to 900° C, RP1797 593
Corundum, heat capacity, RP1797 593
Creamer, Ansel S., Elmer N. Bunting, George R. Shelton, Properties of barium-strontium titanate dielectrics, RP1776 337
Creep, tensile and compressive, of refractory bricks, RP1770 229
Cryoscopic constants of hydrocarbons, RP1760 53
Crystal units, quartz, electrical characteristics, RP1774 309
Curtiss, Leon F., Leonard C. Miller, A magnetic-lens electron spectrometer: Radiations from 5.3 year cobalt ^{60}, RP1778 359
—, *Irving Feister*, Disintegration of scandium ^{46}, RP1781 411
Cyclohexanes, infrared absorption spectra, RP1769 211
Cycloparaffin hydrocarbons, purification, purity, and freezing points, RP1760 53
Cyclopentanes, infrared absorption of, RP1769 211

D

Davis, Francis J., An improved Geiger-counter arrangement for determination of radium content, RP1792 513
Day, Frank H., George Singer, Harold O. Wyckoff, Relative thickness of lead, concrete, and steel required for protection against narrow beams of X-rays, RP1806 665
Diamond-die production, electrical methods, RP1787 449
Dibeler, Vernon H., A. Keith Brewer, Samuel L. Madorsky, John Keenan Taylor, Paul Bradt, O. Lee Parham, Roy J. Britten, J. Gilman Reid, Jr., Concentration of isotopes of potassium by the countercurrent electromigration method, RP1765 137
—, *Fred L. Mohler, Robert M. Reese*, Mass spectrometer study of rare gases, RP1799 617
—, Ionization and dissociation of *cis*- and *trans*-2-butene by electron impact, RP1775 329
Dicalcium silicate, crystal structure, RP1782 415

Page

Die, diamond, electrical methods for production, RP1787 ... 449
Dielectrics properties of barium-strontium titanate, RP1776 ... 337
Difructose anhydride II, structure, RP1784 ... 423
Dimethylcyclohexanes, heat of combustion and isomerization, RP1783 ... 419
2 2-Dimethylhexane in petroleum, RP1800 ... 621
Dipole moments of benzein indicators, RP1791 ... 505

E

Elastic behavior of refractory bricks, RP1770 ... 229
Electrical characteristics of quartz-crystal units, RP1774 ... 309
Electrical methods for diamond-die production, RP1787 ... 449
Electromigration method for the concentration of isotopes:
RP1765 ... 137
RP1766 ... 169
RP1767 ... 185
Electron spectrometer, magnetic-lens, RP1778 ... 359
Emerson, Walter B., Chauncey G. Peters, Karl Nefflen, Frank K. Harris, Irvin L. Cooter, Electrical methods for diamond-die production, RP1787 ... 449
Ethylbenzene, vibrational frequencies, RP1758 ... 1
Ethylcyclohexane, heat of combustion, RP1783 ... 419
Ethylcyclopentane in petroleum, RP1800 ... 621
Ethylene, vibrational frequencies, RP1708 ... 191
Expansion, thermal, of barium-strontium titanate, RP1776 ... 337

F

Fabrics, water-repellent, RP1762 ... 103
Faick, Conrad A., Ralph Stair, Infrared absorption of some experimental glasses containing rare earth and other oxides, RP1761 ... 95
Freezing points, purification, and purity of 8 nonanes, 11 alkylcyclopentanes, 6 alkylcyclohexanes, and 4 butylbenzenes of American Petroleum Institute-National Bureau of Standards series, RP1760 ... 53
Feister, Irving, Leon F. Curtiss, Disintegration of scandium 46, RP1781 ... 411
Ferrite, heats of solution, RP1805 ... 661
Firebrick, creep and elastic behavior, RP1770 ... 229
Flanagan, Helen F., Anton J. Streiff, Evelyn T. Murphy, Janice C. Cahill, Vincent A. Sedlak, Charles B. Willingham, Frederick D. Rossini, Purification, purity, and freezing points of 8 nonanes, 11 alkylcyclopentanes, 6 alkylcyclohexanes, and 4 butylbenzenes of the American Petroleum Institute-Standard and American Petroleum Institute-National Bureau of Standards series, RP1760 ... 53
Fookson, A., Frank L. Howard, Thomas W. Mears, Philip Pomerantz, Donald B. Brooks, Preparation and physical properties of several aliphatic hydrocarbons and intermediates, RP1779 ... 365
Francis, Harold E., Hugh L. Logan, Harold Hessing, Effect of artificial aging on tensile properties and resistance to corrosion of the 24S-T aluminum alloy, RP1788 ... 465
Frequency-modulation demodulator, synchronized oscillator as a, RP1780 ... 397
Furnace for X-ray diffraction at elevated temperatures, RP1782 ... 415

G

Gagliardi, Domenick, John W. Rowen, Properties of water-repellent fabrics, RP1762 ... 103
Gardner, Irvine C., Compensation of the aperture ratio markings of a photographic lens for absorption, reflection, and vignetting losses, RP1803 ... 643
Gases, heat capacities and P-V-T data, RP1804 ... 651
Gases, rare, mass spectrometer study, RP1799 ... 617
Gas, natural, analysis:
RP1759 ... 19
RP1789 ... 491
Geiger-counter, determination of radium content, RP1792 ... 513
George, William D., Myron C. Selby, Reuben Scolnik, Electrical characteristics of quartz-crystal units and their measurement, RP1774 ... 309
Gibson, Kasson S., Margaret M. Balcom, Transmission measurements with the Beckman quartz spectrophotometer, RP1798 ... 601
Giauque, Defoe C., Robert J. Corruccini, An improved ice calorimeter—the determination of its calibration factor and the density of ice at 0° C, RP1796 ... 583
—, —, Enthalpy, specific heat, and entropy of aluminum oxide from 0° to 900° C, RP1797 ... 593
Glasgow, Augustus R., Jr., Anton J. Streiff, Charles B. Willingham, Frederick D. Rossini, Analyses of alkylates and hydrocodimers, RP1795 ... 537

Page

Glasgow, Augustus R., Jr., Charles B. Willingham, Frederick D. Rossini, Hydrocarbons in the 102° to 108° C fraction of petroleum, RP1800 ... 621
Glass, changes in refractivity and density caused by annealing, RP1791 ... 505
Glass in portland cement clinker, estimation, RP1805 ... 661
Glass, optical, surface tensions, RP1771 ... 241

H

Harris, Forest K., Chauncey G. Peters, Walter B. Emerson, Karl Nefflen, Irvin L. Cooter, Electrical method for diamond-die production, RP1787 ... 449
Harrison, William N., Dwight G. Moore, Joseph C. Richmond, Ceramic coatings for high-temperature protection of steel, RP1773 ... 259
Heat capacity of aluminum oxide, RP1797 ... 593
Heat capacity of gases, RP1804 ... 651
Heats of combustion and solution of styrene and polystyrene, RP1801 ... 627
Heats of polymerization of styrene, RP1801 ... 627
Heats of combustion and isomerization of six nonanes, RP1783 ... 419
Helz, Armin W., Bourdon F. Scribner, Spectrographic determination of minor elements in portland cement, RP1786 ... 439
Hessing, Harold, Hugh L. Logan, Harold E. Francis, Effect of artificial aging on the tensile properties and resistance to corrosion of the 24S-T aluminum alloy, RP1788 ... 465
Hide, adsorption of water vapor, RP1763 ... 119
High-temperature X-ray diffraction apparatus, RP1782 ... 415
Howard, Frank L., Thomas W. Mears, A. Fookson, Philip Pomerantz, Donald B. Brooks, Preparation and physical properties of several aliphatic hydrocarbons and intermediates, RP1779 ... 365
Humphreys, Curtis J., Earle K. Plyler, Infrared emission of spectra of krypton and argon, RP1790 ... 499
—, —, *Ralph Stair*, Infrared absorption spectra of twelve cyclopentanes and five cyclohexanes, RP1769 ... 211
Huntoon, Robert D., Albert Weiss, Synchronization of oscillators, RP1780 ... 397
Hydrocarbons, aliphatic, preparation and properties, RP1779 ... 365
Hydrocarbons, infrared absorption spectra, RP1769 ... 211
Hydrocarbons in alkylates and hydrocodimers, RP1795 ... 537
Hydrocarbons in petroleum, RP1800 ... 621
Hydrocodimers, analysis, RP1795 ... 537

I

Ice, density at 0° C, RP1796 ... 583
Infrared absorption spectra of some hydrocarbons, RP1769 ... 211
Infrared absorption spectra of rare-earth oxide glasses, RP1761 ... 95
Infrared emission spectra of krypton and argon, RP1790 ... 499
Inulin, difructoses prepared from, RP1784 ... 423
Ionization of *cis-* and *trans*-2-butene, RP1775 ... 329
Isobutane, heat capacities, RP1804 ... 651
Isotopes, concentration of potassium:
RP1765 ... 137
RP1766 ... 169
Isotopes of chlorine, concentration by the countercurrent electromigration method, RP1767 ... 185
Isotopes of mercury, concentration by free evaporation, RP1764 ... 129
Isotopes, theoretical aspects of the electromigration method for concentrating, RP1766 ... 169

J

Jessup, Ralph S., Donald E. Roberts, William W. Walton, Heats of combustion and solution of liquid styrene and solid polystyrene, and the heat of polymerization of styrene, RP1801 ... 627
Johnson, Walter H., Edward J. Prosen, Frederick D. Rossini, Heats of combustion and isomerization of six nonanes, RP1783 ... 419

K

Kanagy, Joseph R., Adsorption of water vapor by untanned hide and various leathers at 100° F, RP1763 ... 119
Kilpatrick, John E., Kenneth S. Pitzer, Normal coordinate analysis of the vibrational frequencies of ethylene, propylene, *cis*-2-butene, *trans*-2-butene, and isobutene, RP1768 ... 191
Kinetic-energy matrix, calculation, RP1758 ... 1
Krypton and argon, infrared emission spectra, RP1790 ... 499

L

Page

Laminar boundary layer flow, RP1772 ... 251
Latex, Mangabeira, RP1785 ... 427
Leather, adsorption of water vapor, RP1763 ... 119
Lens, compensation for absorption, reflection, and vignetting losses by aperture ratio markings, RP1803 ... 643
Logan, Hugh L., Harold Hessing, Harold E. Francis, Effect of artificial aging on the tensile properties and resistance to corrosion of the 24S–T aluminum alloy, RP1788 ... 465

M

Madorsky, Samuel L., A. Keith Brewer, Concentration of the isotopes of mercury by free evaporation in a 10-cell countercurrent reflux still, RP1764 ... 129
—, —, *John Keenan Taylor, Vernon H. Dibeler, Paul Bradt, O. Lee Parham, Roy J. Britten, J. Gilman Reid, Jr.*, Concentration of isotopes of potassium by the countercurrent electromigration method, RP1765 ... 137
—, *Sidney Straus*, Concentration of isotopes of chlorine by the countercurrent electromigration method, RP1767 ... 185
Magnetic-lens electron spectrometer, RP1778 ... 559
Mangabeira latex and rubber, RP1785 ... 427
Maryott, Arthur A., Conductimetric titrations of acids and bases in benzene and dioxane, RP1794 ... 527
—, *S. Acree*, Dipole moments and resonance of some benzein indicators and related compounds, RP1791 ... 505
Mass spectrometer analysis of standard natural gas sample, RP1789 ... 491
Mass spectrometer study of rare gases, RP1799 ... 617
Mass spectrometric analysis:
RP1765 ... 137
RP1767 ... 185
Mass spectrometric analysis of potassium isotopes abundance ratio, RP1765 ... 137
McDonald, Emma J., Anne L. Turcotte, Structure of difructose anhydride II, RP1784 ... 423
McMurdie, Howard F., Alvin Van Valkenburg, Jr., High-temperature X-ray diffraction apparatus, RP1782 ... 415
Mears, Thomas W., Frank L. Howard, A. Fookson, Philip Pomerantz, Donald D. Brooks, Preparation and physical properties of several aliphatic hydrocarbons and intermediates, RP1779 ... 365
Mercury isotopes, concentration by free evaporation, RP1764 ... 129
Miller, Leonard C., Leon F. Curtiss, A magnetic-lens electron spectrometer: Radiations from 5.3 year cobalt,[58] RP1778 ... 359
Mohler, Fred L., Vernon H. Dibeler, Robert M. Reese, Mass spectrometer study of rare gases, RP1799 ... 617
Mong, Lewis E., Elastic behavior and creep of refractory bricks under tensile and compressive loads, RP1770 ... 229
Moore, Dwight G., William N. Harrison, Joseph C. Richmond, Ceramic coatings for high-temperature protection of steel, RP1773 ... 293
Murphy, Evelyn T., Anton J. Streiff, Janice C. Cahill, Helen F. Flanagan, Vincent A. Sedlak, Charles B. Willingham, Frederick D. Rossini, Purification, purity, and freezing points of 8 nonanes, 11 alkylcyclopentanes, 6 alkylcyclohexanes, and 4 butylbenzenes of the American Petroleum Institute-Standard and American Petroleum Institute-National Bureau of Standards series, RP1760 ... 53

N

Natural gas, analysis:
RP1759 ... 19
RP1789 ... 491
Neffen, Karl, Chauncey G. Peters, Walter B. Emerson, Forest K. Harris, Irvin L. Cooter, Electrical methods for diamond-die production, RP1787 ... 449
Newman, Edwin S., Heats of solution of solid solutions of hexacalcium dialumino ferrite and dicalcium ferrite, RP1805 ... 661
Nonanes, purification, purity, and freezing points, RP1760 ... 53
Normal coordinate analysis of olefins, RP1768 ... 191
Nuclear energy levels of cobalt, RP1778 ... 359
Nuclear energy levels of scandium [46], RP1781 ... 411

O

Olefins, vibrational frequencies, RP1768 ... 191
Optical glass, surface tensions, RP1771 ... 241
Oscillations in laminar boundary layers, RP1772 ... 251
Oscillators, synchronization of, RP1780 ... 397
Oxygen, heat capacities, RP1804 ... 651

P

Page

Paraffin hydrocarbons, purification, purity, and freezing points, RP1760 ... 53
Parham, O. Lee, A. Keith Brewer, Samuel L. Madorsky, John Keenan Taylor, Vernon H. Dibeler, Paul Bradt, Roy J. Britten, J. Gilman Reid, Jr., Concentration of isotopes of potassium by the countercurrent electromigration method, RP1765 ... 137
Peters, Chauncey G., Walter B. Emerson, Karl Neffen, Frank K. Harris, Irvin L. Cooter, Electrical methods for diamond-die production, RP1787 ... 449
Petroleum, hydrocarbons in, RP1800 ... 621
Photographic lens, compensation of the aperture ratio markings for absorption, reflection, and vignetting losses, RP1803 ... 643
Pitzer, Kenneth S., John E. Kilpatrick, Normal coordinate analysis of the vibrational frequencies of ethylene, propylene, *cis*-2-butene, *trans*-2-butene, and isobutene, RP1768 ... 191
—, *William J. Taylor*, The vibrational frequencies of semirigid molecules: A general method and values for ethylbenzene, RP1758 ... 1
Plyler, Earle K., Curtis J. Humphreys, Infrared emission of spectra of krypton and argon, RP1790 ... 499
—, *Ralph Stair, Curtis J. Humphreys*, Infrared absorption spectra of seven cyclopentanes and five cyclohexanes, RP1769 ... 211
Polystyrene and styrene, heats of combustion and solution, RP1801 ... 627
Pomerantz, Philip, Frank L. Howard, Thomas W. Mears, A. Fookson, Donald D. Brooks, Preparation and physical properties of several aliphatic hydrocarbons and intermediates, RP1779 ... 365
Portland cement clinker, estimation of glass in, RP1805 ... 661
Portland cement, spectrographic analysis, RP1786 ... 439
Potassium isotopes, concentration:
RP1765 ... 137
RP1766 ... 169
Potentials, critical of *cis*- and *trans*-2-butene, RP1775 ... 329
Propylene, vibrational frequencies, RP1768 ... 191
Prosen, Edward J., Walter H. Johnson, Frederick D. Rossini, Heats of combustion and isomerization of six nonanes, RP1783 ... 419
Purification and purity of hydrocarbons, RP1760 ... 53

Q

Quartz-crystal units, electrical measurements, RP1774 ... 309

R

Radium content, determination, RP1792 ... 513
Rare-earth oxide glasses, infrared absorption, RP1761 ... 95
Reese, Robert M., Vernon H. Dibeler, Fred L. Mohler, Mass spectrometer study of rare gases, RP1799 ... 617
Reflection losses of a photographic lens, compensation by aperture ratio markings, RP1803 ... 643
Reflux control for electromigration cells, RP1765 ... 137
Refractivity of glass, changes caused by annealing, RP1793 ... 519
Refractory bricks, creep and elastic behavior, RP1770 ... 229
Reid, J. Gilman, Jr., A. Keith Brewer, Samuel L. Madorsky, John Keenan Taylor, Vernon H. Dibler, Paul Bradt, O. Lee Parham, Roy J. Britten, Concentration of isotopes of potassium by the countercurrent electromigration method, RP1765 ... 137
Resonance in benzein indicators, RP1791 ... 505
Richmond, Joseph C., William N. Harrison, Dwight G. Moore, Ceramic coatings for high-temperature protection of steel, RP1773 ... 293
Rivlin, Ronald S., Torsion of a rubber cylinder, RP1802 ... 637
Roberts, Donald E., William W. Walton, Ralph S. Jessup, Heats of combustion and solution of liquid styrene and solid polystyrene and the heat of polymerization of styrene, RP1801 ... 627
Rossini, Frederick D., Anton J. Streiff, Evelyn T. Murphy Janice C. Cahill, Helen F. Flanagan, Vincent A. Sedlak, Charles B. Willingham, Purification, purity, and freezing points of 8 nonanes, 11 alkylcyclopentanes, 6 alkycyclohexanes, and 4 butylbenzenes of the American Petroleum Institute-Standard and American Petroleum Institute-National Bureau of Standards series, RP1760 ... 53
—, *Augustus R. Glasgow, Jr., Anton J. Streiff, Charles B. Willingham*, Analysis of alkylates and hydrocodimers, RP1795 ... 537
—, —, *Charles B. Willingham*, Hydrocarbons in the 102° to 108° C fraction of petroleum, RP1800 ... 621
—, *Walter H. Johnson, Edward J. Prosen*, Heats of combustion and isomerization of six nonanes, RP1783 ... 419

Page

Rowen, John W., Domenick Gagliardi, Properties of water-repellent fabrics, RP1762 103
Rubber cylinder, torsion of, RP1802 637
Rubber, Mangabeira, RP1785 427

S

Saffiati, Waldemar, Norman Bekkedahl, Mangabeira latex and rubber, RP1785 427
Sapphire, heat capacity, RP1797 593
Saunders, James B., Arthur Q. Tool, Leroy W. Tilton, Changes caused in the refractivity and density of glass by annealing, RP1793 519
Schubauer, Galen B., Harold K. Skramstad, Laminar boundary-layer oscillations and transition on a flat plate, RP1772 251
Scolnik, Reuben, William D. George, Myron C. Selby, Electrical characteristics of quartz-crystal units and their measurement, RP1774 309
Scott, Russell B., Paul F. Wacker, Ruth K. Cheney, Heat capacities of gaseous oxygen, isobutane, and 1-butene from −30° to +90° C, RP1804 651
Scribner, Bourdon F., Armin W. Helz, Spectrographic determination of minor elements in portland cement, RP1786 439
Sedlak, Vincent A., Anton J. Streiff, Evelyn T. Murphy, Janice C. Cahill, Helen F. Flanagan, Charles B. Willingham, and Frederick D. Rossini, Purification, purity, and freezing points of 8 nonanes, 11 alkylcyclopentanes, 6 alkylcyclohexanes, and 4 butylbenzenes of the American Petroleum Institute-Standard and American Petroleum Institute-National Bureau of Standards series, RP1760 53
Selby, Myron C., William D. George, Reuben Scolnik, Electrical characteristics of quartz-crystal units and their measurements, RP1774 309
Shartsis, Leo, Alden W. Smock, Surface tensions of some optical glasses, RP1771 241
Shelton, George R., Elmer N. Bunting, Ansel S. Creamer, Properties of barium-strontium titanate dielectrics, RP1776 337
Shepherd, Martin, Analysis of a standard sample of natural gas by laboratories cooperating with the American Society for testing materials, RP1759 19
—, Cooperative analysis of a standard sample of natural gas with the mass spectrometer, RP1789 491
—, Determination of small amounts of carbon monoxide in air by various reference methods, RP1777 351
Singer, George, Harold O. Wyckoff, Frank H. Day, Relative thickness of lead, concrete, and steel required for protection against narrow beams of X-rays, RP1806 665
Skramstad, Harold K., Galen B. Schubauer, Laminar boundary-layer oscillations and transition on a flat plate, RP1772 251
Smock, Alden W., Leo Shartsis, Surface tensions of some optical glasses, RP1771 241
Specific heat of aluminum oxide, RP1797 593
Spectra, beta and gamma ray, of scandium ^{46}, RP1781 411
Spectra, infrared absorption, of hydrocarbons, RP1769 211
Spectra, mass, of *cis-* and *trans-*2-butene, RP1775 329
Spectra of noble gases, RP1790 499
Spectrographic analysis of portland cement, RP1786 439
Spectrophotometer, Beckman, performance, RP1798 601
Stair, Ralph, Conrad A. Faick, Infrared absorption of some experimental glasses containing rare earth and other oxides, RP1761 95
—, *Earle K. Plyler, Curtis J. Humphreys,* Infrared absorption spectra of seven cyclopentanes and five cyclohexanes, RP1769 211
Steel, high-temperature protective coatings, RP1773 293
Straus, Sidney, Samuel L. Madorsky, Concentration of isotopes of chlorine by the countercurrent electromigration method, RP1767 185
Streiff, Anton J., Augustus R. Glasgow, Jr., Charles B. Willingham, Frederick D. Rossini, Analyses of alkylates and hydrocodimers, RP1795 537
—, *Evelyn T. Murphy, Janice C. Cahill, Helen F. Flanagan, Vincent A. Sedlak, Charles B. Willingham, Frederick D. Rossini,* Purification, purity, and freezing points of 8 nonanes, 11 alkylcyclopentanes, 6 alkylcyclohexanes, and 4 butylbenzenes of the American Petroleum Institute-Standard and American Petroleum Institute-National Bureau of Standards series, RP1760 53
Stress-corrosion tests of aluminum alloy, RP1788 465
Surface tension of some optical glasses, RP1771 241

T

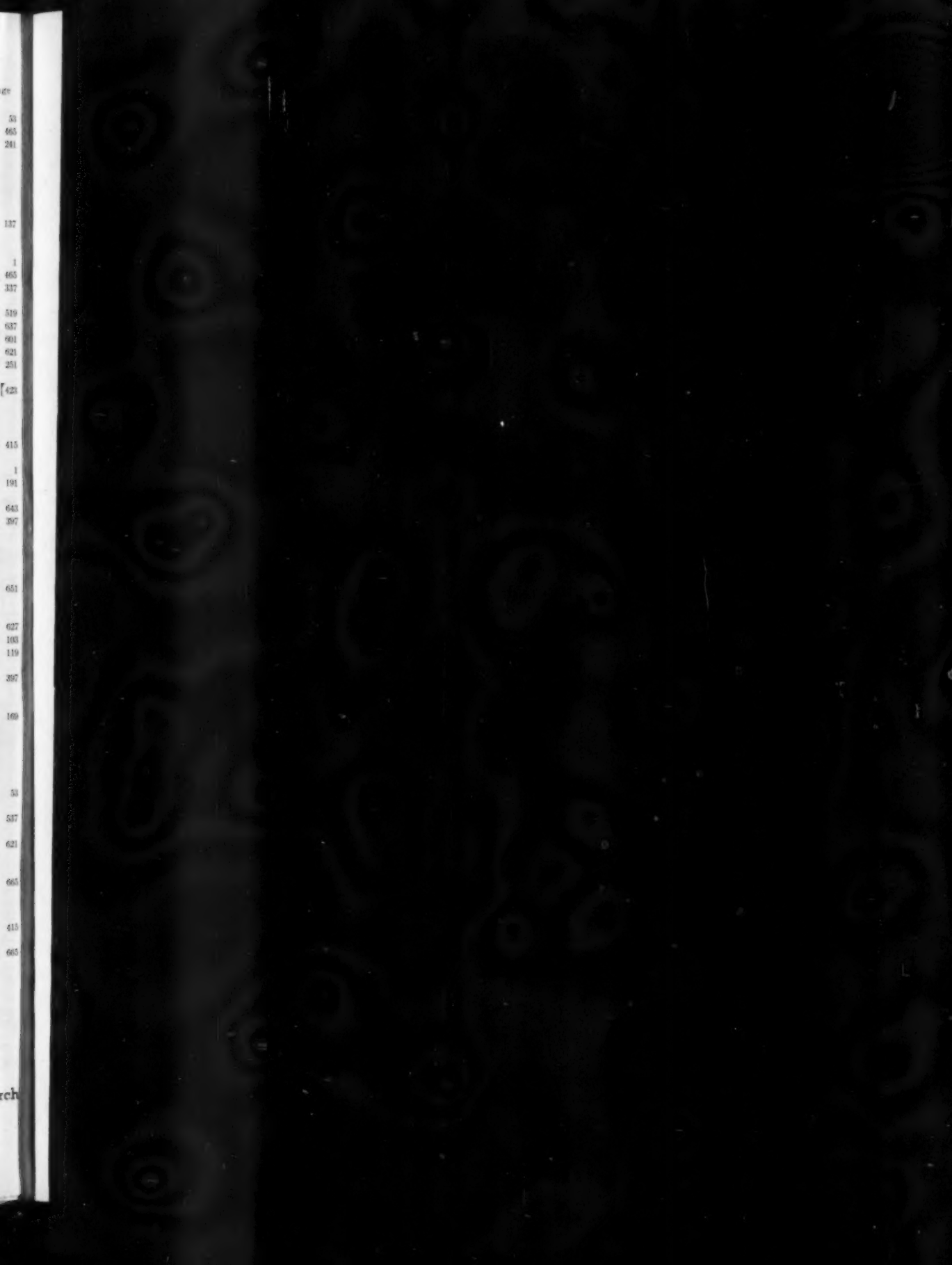
Taylor, John Keenan, A. Keith Brewer, Samuel L. Madorsky, Vernon H. Dibeler, Paul Bradt, O. Lee Parham, Roy J. Britten, J. Gilman Reid, Jr., Concentration of isotopes of potassium by the countercurrent electromigration method, RP1765 137
Taylor, William J., Kenneth S. Pitzer, Vibrational frequencies of semi-rigid molecules: A general method and values for ethylbenzene, RP1758 1
Tensile properties of aluminum alloy, RP1788 465
Thermal expansion for barium-strontium titanate, RP1776 337
Tilton, Leroy W., Arthur Q. Tool, James B. Saunders, Changes caused in the refractivity and density of glass by annealing, RP1793 519
Torsion of a rubber cylinder, RP1802 637
Transmission measurements on Beckman spectrophotometer, RP1798 601
1,1,3-Trimethylcyclopentane in petroleum, RP1800 621
Turbulence, boundary layer, production of, RP1772 251
Turcotte, Anne L., Emma J. McDonald, Structures of difructose anhydride II, RP1784 423

V

Van Valkenburg, Alvin, Jr., Howard F. McMurdie, High-temperature X-ray diffraction apparatus, RP1782 415
Vibrational frequencies of molecules:
RP1758 1
RP1768 191
Vignetting losses of a photographic lens, compensation by aperature ratio markings, RP1803 643
Voltmeter, synchronized oscillator as a, RP1780 397

W

Wacker, Paul F., Ruth K. Cheney, Russell B. Scott, Heat capacities of gaseous oxygen, isobutane, and 1-butene from −30° to +90° C, RP1804 651
Walton, William W., Donald E. Roberts, Ralph S. Jessup, Heats of combustion and solution of liquid styrene and solid polystyrene, and the heat of polymerization of styrene, RP1801 627
Water repellency of fabrics, RP1762 103
Water vapor adsorption of leather, RP1763 119
Weiss, Albert, Robert D. Huntoon, Synchronization of oscillators, RP1780 397
Westhaver, James W., Concentration of potassium ^{39} by countercurrent electromigration: Some theoretical aspects of the operation, RP1766 169
Willingham, Charles B., Anton J. Streiff, Evelyn T. Murphy, Janice C. Cahill, Helen F. Flanagan, Vincent A. Sedlak, Frederick D. Rossini, Purification, purity, and freezing points of 8 nonanes, 11 alkylcyclopentanes, 6 alkylcyclohexanes, and 4 butylbenzenes of the American Petroleum Institute-Standard and American Petroleum Institute-National Bureau of Standards series, RP1760 53
—, *Augustus R. Glasgow, Jr., Anton J. Streiff, Frederick D. Rossini,* Analysis of alkylates and hydrocodimers, RP1795 537
—, —, *Frederick D. Rossini,* Hydrocarbons in the 102° to 108° C fraction of petroleum, RP1800 621
Wyckoff, Harold O., George Singer, Frank H. Day, Relative thickness of lead, concrete, and steel required for protection against narrow beams of X-rays, RP1806 665

X

X-ray diffraction at elevated temperatures, RP1782 415
X-ray protection, thickness of lead, concrete, and steel required, RP1806 665